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

Supporting information

Cycloreversion performance of coumarin and hetero-coumarin dimers under aerobic conditions: unexpected behavior triggered by UV-A light

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1 Experimental procedure

1.1 Dimerization Reactions

The dimerization reactions were performed in an air-cooled Rayonet-type photoreactor equipped with 16 CLEO PERFORMANCE 40W R UV fluorescent tubes ($\lambda_{em,\,max}$ = 350 nm, Figure S 1). For the head-to-head-dimers of coumarin-containing molecules, degassed acetonitrile solutions of the monomers (0.1 – 0.5 M) containing 15 mol% benzophenone were irradiated. For the head-to-tail dimers, 1 eq of boron trifluoride diethyl etherate was added to degassed solutions of the monomers (0.1 – 0.5 M) in acetonitrile or dichloromethane. The head-to-head dimers of 1-methyl-quinolinone and 1,1-dimethyl-naphtalenone containing monomer were synthesized by irradiation

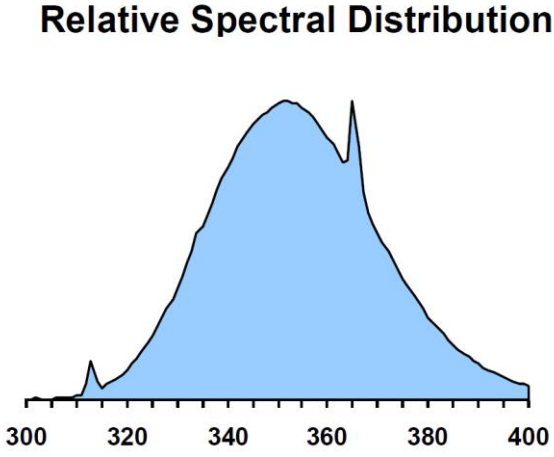

Figure S 1: Emission spectrum of the utilized fluorescent tubes in the Rayonet-type batch reactor (ID: FR24 T12 40W-K PH).

of 0.5 M degassed solutions in acetonitrile without the addition of any photosensitizer. All dimers were purified by recrystallization from acetonitrile.

1.2 High-Performance Liquid Chromatography

The synthesis reactions were monitored via HPLC using an ULTIMATE 3000 system (DIONEX) with a diode array detector. An RP-18 column (BISCHOFF CHROMATOGRAFIE) was used with a 60:40 (v/v) or 75:25 (v/v) mixture of acetonitrile and water (acidified with 300 µL H_3PO_4 /L) as the eluent at a flow rate of 1 mL/min.

1.3 NMR spectroscopy

^{1}H- and ^{13}C-NMR spectra were measured on an AV-300 (BRUKER, 300 MHz) or an AV-500 (BRUKER, 500 MHz) using dimethyl sulfoxide-d_6 or chloroform-*d* as solvent. The δ chemical shift scale was calibrated using the residual solvent peak.

1.4 Mass spectrometry

HR-ESI mass spectra were acquired with an LTQ-FT ULTRA mass spectrometer (THERMO FISCHER SCIENTIFIC) using acetonitrile as solvent.

1.5 Chemicals

Coumarin (**1c**) (ACROS ORGANICS, 99+%), 7-methyl-coumarin (**2c**) (SIGMA ALDRICH, 98+%) and 7-methoxy-coumarin (**3c**) (ALFA AESAR, 98+%) were commercially available. All other monomers were synthesized from the following starting materials: malic acid (ALFA AESAR, 99%), 3-fluorophenol (SIGMA ALDRICH, 98%), cinnamic acid chloride (ACROS ORGANICS, 98%), *N*-Methylaniline (VWR, 99%), triethylamine (VWR, tech.), aluminum chloride (ROTH, 98%), 7 hydroxyquinoline-2(1*H*)-one (ACCEL PHARMA, 99%), sodium hydride (60% in paraffin oil, SIGMA ALDRICH), methyl iodide (ALFA AESAR, 99%), 1-bromonaphtalen-2-ol (ACROS ORGANICS, 98%), chloromethyl methyl ether (CARBOLUTION, 95%), *n*-butyllithium (2.5 M in hexane, ACROS ORGANICS), 7-methoxy-2-tetralone (ACROS ORGANICS, 95%), tetrabutylammonium-tetrafluoroborate (FLUROCHEM), 2-iodobenzoeic acid (SIGMA ALDRICH, 98%), potassium peroxymonosulfate (SIGMA ALDRICH, tech.). For the dimerization reactions, benzophenone (ALFA AESAR, 99%) or boron trifluoride diethyl etherate (ACROS ORGANICS, ca. 48%) were used. All other chemicals were of at least technical grade. For water-sensitive reactions, dry solvents were used. All other solvents were of technical grade and distilled before use.

1.6 Synthesis of the monomeric compounds

*7-fluoro-2H-chromen-2-one (**4c**)*: 7-fluoro-coumarin was synthesized by dissolving 1.20 g malic acid (8.92 mmol, 1.0 eq.) and 0.81 mL 3-fluorophenol (8.92 mmol, 1.0 eq.) in 2.40 mL conc. H_2SO_4. The mixture was heated to 120 °C for 6 hours. After cooling to room temperature, the residue was poured into 20 mL of ice water. The resulting orange solid was filtered off and washed with water. The solid was dissolved in dichloromethane and adsorbed on silica gel. Column chromatography using methyl *tert*-butyl ether:pentane 1:3 as eluent yielded 583 mg of a colorless solid (1.78 mmol, 20%). Analytics were in accordance with the literature.[S1]

*1-methyl quinoline-2(1H)-one Q (**5c**)*: NMQ was synthesized as published in the literature, starting from cinnamic acid chloride and *N*-Methylaniline.[S2]

*7-methoxy-1-methyl quinoline-2(1H)-one MeOQ (**6c**)*: 10.0 g 7-hydroxyquinoline-2(1*H*)-one (62.1 mol, 1.0 eq.) were dissolved in 300 mL dry DMF. After cooling to 0 °C, 5.4 g NaH (60% in paraffin oil, 136.6 mmol, 2.2 eq.) were added in portions. After 30 min stirring at 0 °C, 8.5 mL MeI (136.6 mmol, 2.2 eq.) was added dropwise. The yellow solution was stirred overnight at room temperature. The solvent was distilled off under reduced pressure. To the resulting solid, water and EtOAc were added. The phases were separated and the organic phase was washed repeatedly with water. After washing with brine and drying over $MgSO_4$, the organic phase was evaporated to dryness. The residue was adsorbed on silica gel and purified via column chromatography using pentane/MTBE 1:1 to pure ethyl acetate as solvent. The product containing fractions were collected and the solvent was removed, resulting in 10.8 g (57.1 mmol, 92%) of MOQ (**6**) as a colorless solid. Analytics were in accordance with the literature.[S3]

*1,1-dimethylnaphtalen-2(1H)-one N (**7c**)*: DMN was synthesized as published in the literature, starting from 1-bromonaphtalen-2-ol.[S4]

*7-methoxy-1,1-dimethylnaphtalen-2(1H)-one MON (**8c**)*: MON (**8c**) was synthesized in a slightly modified literature procedure, using tetrabutylammonium-tetrafluoroborate instead of tetrabutylammonium sulfate.[S5] Oxidation was done as published before, using IBX in DMSO/toluene.[S6]

1.7 Analytics of the dimeric compounds

*anti-head-to-head coumarin dimer (hh-C (**1a**))*: ^{1}H-NMR (300 MHz, DMSO-d_6): δ = 3.86-3.97 (m, 4H, $H_{cyclobutane}$), 7.10-7.14 (m, 2H, H_{Ar}), 7.19-7.25 (m, 2H, H_{Ar}), 7.34-7.40 (m, 2H, H_{Ar}) *ppm*. ^{13}C-NMR (75 MHz, DMSO-d_6): δ = 39.0, 42.6, 117.0, 121.5, 125.1, 128.6, 129.0, 150.6, 165.7 *ppm*. HRMS (ESI+, ACN): calc. for $C_{18}H_{12}O_4H^+$: 293.0808, found 293.0811.

*syn-head-to-tail coumarin dimer (ht-C (**1b**))*: ^{1}H-NMR (300 MHz, DMSO-d_6): δ = 4.21-4.34 (m, 4H, $H_{cyclobutane}$), 6.613 (dd, 2H, ^{3}J = 8.0 Hz, ^{4}J = 1.4 Hz, H_{Ar}), 7.01-717. (m, 6H, H_{Ar}) *ppm*. ^{13}C-NMR (75 MHz, DMSO-d_6): δ = 37.1, 40.2, 116.3, 118.4, 124.4, 128.8, 129.1, 150.5, 163.9 *ppm*. HRMS (ESI+, ACN): calc. for $C_{18}H_{12}O_4Na^+$: 315.0632, found 315.0628.

*anti-head-to-head 7-methyl-coumarin dimer (hh-MeC (**2a**))*: ^{1}H-NMR (300 MHz, C*D*Cl$_3$): δ = 2.37 (s, 6H, Ar-CH_3), 3.76-3.91 (m, 4H, $H_{cyclobutane}$), 6.93-7.03 (m, 6H, H_{Ar}) *ppm*. ^{13}C-NMR (75 MHz, C*D*Cl$_3$): δ = 21.3, 40.3, 43.9, 117.5, 118.3, 126.3, 127.7, 140.3, 151.2, 166.4 *ppm*. HRMS (ESI+, ACN): calc. for $C_{20}H_{16}O_4Na^+$: 343.0941, found 343.3940.

*syn-head-to-tail 7-methyl-coumarin dimer (ht-MeC (**2b**))*: ^{1}H-NMR (300 MHz, DMSO-d_6): δ = δ = 2.19 (s, 6H, Ar-CH_3), 4.20-4.25 (m, 4H, $H_{cyclobutane}$), 6.51 (s, 2H, H_{Ar}), 6.91 (s, 4H, H_{Ar}) *ppm*. ^{13}C-NMR (75 MHz, DMSO-d_6): δ = 20.5, 35.6, 115.2, 116.6, 125.2, 128.8 138.8, 150.4, 164.1 *ppm*. HRMS (ESI+, ACN): calc. for $C_{20}H_{16}O_4Na^+$: 343.0941, found 343.3945.

*syn-head-to-head 7-methoxy-coumarin dimer (hh-MeOC (**3a**))*: ^{1}H-NMR (300 MHz, DMSO-d_6): δ = 3.70-3.89 (m, 4H, $H_{cyclobutane}$), 3.78 (s, 6H, OCH_3), 6.71 (d, ^{4}J = 2.5 Hz, 2H, H_{Ar}), 6.81 (dd, ^{3}J = 8.5 Hz, ^{4}J = 2.5 Hz, 3H, H_{Ar}), 7.28 (d, ^{3}J = 8.5 Hz, 2H, H_{Ar}) *ppm*. ^{13}C-NMR (75 MHz, DMSO-d_6): δ = 38.7, 42.2, 55.5, 102.1, 111.45, 113.3, 129.3, 151.4, 159.7, 165.7 *ppm*. HRMS (ESI+, ACN): calc. for $C_{20}H_{16}O_6H^+$: 353.1020, found 353.1023.

*syn-head-to-tail 7-methoxy-coumarin dimer (ht-MeOC (**3b**))*: ^{1}H-NMR (300 MHz, DMSO-d_6): δ = 3.67 (s, 6H, OCH_3), 4.15-4.26 (m, 4H, $H_{cyclobutane}$), 6.29 (d, ^{4}J = 2.5 Hz, 2H, H_{Ar}), 6.70 (dd, ^{3}J = 8.6 Hz, ^{4}J = 2.5 Hz, 3H, H_{Ar}), 6.94 (d, ^{3}J = 8.6 Hz, 2H, H_{Ar}) *ppm*. ^{13}C-NMR (75 MHz, DMSO-d_6): δ = 36.3, 39.9, 55.4, 101.6, 110.1, 110.9, 129.7, 151.4, 159.6, 164.1 *ppm*. HRMS (ESI+, ACN): calc. for $C_{20}H_{16}O_6Na^+$: 375.0844, found 375.0839.

*syn-head-to-head 7-fluoro-coumarin dimer (hh-FC (**4a**))*: ^{1}H-NMR (300 MHz, DMSO-d_6): δ = 3.82-3.98 (m, 4H, $H_{cyclobutane}$), 7.07-7.12 (m, 4H, H_{Ar}), 7.43-7.48 (m, 2H, H_{Ar}) *ppm*. ^{13}C-NMR (75 MHz, DMSO-d_6): δ = 38.5, 42.0, 104.5 (d, ^{2}J = 25.4 Hz), 112.0 (d, ^{2}J = 21.4 Hz), 117.7 (d, ^{4}J = 3.3 Hz), 130.3 (d, ^{3}J = 9.6 Hz), 151.4 (d, ^{3}J = 12.3 Hz), 161.7 (d, ^{1}J = 242.9 Hz), 165.1 *ppm*. HRMS (ESI+, ACN): calc. for $C_{18}H_{10}O_4F_2H^+$: 329.0620, found 329.0619.

*syn-head-to-tail 7-fluoro-coumarin dimer (ht-FC (**4b**))*: ^{1}H-NMR (300 MHz, DMSO-d_6): δ = 4.24-4.27 (m, 4H, $H_{cyclobutane}$), 6.67-6.71 (dd, ^{2}J = 2.5 Hz, ^{3}J = 9.8 Hz, 2H, H_{Ar}), 6.96-7.10 (m, 4H, H_{Ar}) *ppm*. ^{13}C-NMR (75 MHz, DMSO-d_6): δ = 36.6, 40.0, 103.9 (d, ^{2}J = 25.3 Hz), 111.6 (d, ^{2}J = 21.6 Hz), 114.8 (d, ^{4}J = 3.4 Hz), 130.5 (d, ^{3}J = 9.8 Hz), 151.4 (d, ^{3}J = 12.1 Hz), 161.7 (d, ^{1}J = 243.3

Hz), 163.4 *ppm*. HRMS (ESI+, ACN): calc. for $C_{20}H_{14}O_4F_2NH^+$: 370.0885, found 370.087 (ACN adduct).

*anti-head-to-head NMQ dimer (hh-Q (**5a**))*: ^{1}H-NMR (300 MHz, DMSO-d_6): δ = 3.36 (s, 6H, NCH_3), 3.49-3.59 (m, 2H, $H_{cyclobutane}$), 3.78-3.87 (m, 2H, $H_{cyclobutane}$), 6.89 (dd, ^{3}J = 7.4 Hz, ^{4}J = 1.4 Hz, 2H, H_{Ar}), 7.00 (dt, ^{3}J = 7.4 Hz, ^{4}J = 0.8 Hz, 2H, H_{Ar}), 7.14 (d, 2H, ^{3}J = 8.1 Hz, H_{Ar}), 7.31 (dt, ^{3}J = 8.1 Hz, ^{4}J = 1.4 Hz, 2H, H_{Ar}) *ppm*. ^{13}C-NMR (75 MHz, DMSO-d_6): δ = 29.2, 42.8, 43.3, 115.2, 122.8, 123.4, 127.5, 128.2, 139.3, 168.3 *ppm*. HRMS (ESI+, ACN): calc. for $C_{20}H_{18}O_2N_2H^+$: 319.1441, found 319.1445.

*anti-head-to-head 7-methoxy-NMQ dimer (hh-MeOQ (**6a**))*: ^{1}H-NMR (300 MHz, DMSO-d_6): δ = 3.34 (s, 6H, NCH_3), 3.45-3.51 (m, 2H, $H_{cyclobutane}$), 3.65-3.70 (m, 2H, $H_{cyclobutane}$), 6.59 (dd, ^{3}J = 8.5 Hz, ^{4}J = 2.4 Hz, 2H, H_{Ar}), 6.66 (d, ^{4}J = 2.4 Hz, 2H, H_{Ar}), 6.81 (d, ^{3}J = 8.5 Hz, 2H, H_{Ar}) *ppm*. ^{13}C-NMR (125 MHz, DMSO-d_6): δ = 29.4, 42.9, 43.0, 55.3, 102.5, 107.2, 115.9, 128.3, 140.4, 159.3, 168.6 *ppm*. HRMS (ESI+, ACN): calc. for $C_{22}H_{28}O_2N_2H^+$: 379.1652, found 379.1656.

*anti-head-to-head DMN dimer (hh-N (**7a**))*: ^{1}H-NMR (300 MHz, DMSO-d_6): δ = 1.33 (s, 6H, CCH_3), 1.47 (s, 6H, CCH_3), 3.66-3.75 (m, 2H, $H_{cyclobutane}$), 4.18-4.28 (m, 2H, $H_{cyclobutane}$), 6.84 (d, ^{4}J = 2.6 Hz, 2H, H_{Ar}) *ppm*. ^{13}C-NMR (75 MHz, DMSO-d_6): δ = 21.0, 27.7, 41.5, 47.1, 47.2, 124.9, 127.3, 127.5, 127.6, 137.0, 143.1, 212.8 *ppm*. HRMS (ESI+, ACN): calc. for $C_{24}H_{24}O_2Na^+$: 367.1669, found 367.1670.

*anti-head-to-head 7-methoxy-DMN dimer (hh-MeON (**8a**))*: ^{1}H-NMR (300 MHz, DMSO-d_6): δ = 1.31 (s, 6H, CCH_3), 1.44 (s, 6H, CCH_3), 3.69-3.68 (m, 2H, $H_{cyclobutane}$), 3.78 (s, 6H, OCH_3), 3.98-4.07 (m, 2H, $H_{cyclobutane}$), 6.84 (d, ^{4}J = 2.6 Hz, 2H, H_{Ar}), 6.98 (dd, ^{3}J = 8.6 Hz, ^{4}J = 2.6 Hz, 2H, H_{Ar}), 6.84 (d, ^{3}J = 8.6 Hz, 2H, H_{Ar}) *ppm*. ^{13}C-NMR (75 MHz, DMSO-d_6): δ = 21.0, 27.8, 41.5, 46.8, 47.2, 55.2, 110.4, 113.1, 127.4, 129.0, 144.6, 158.7, 212.7 *ppm*. HRMS (ESI+, ACN): calc. for $C_{26}H_{28}O_4H^+$: 427.1888, found 427.1880.

2 UV/Vis absorption spectra of all compounds in the study

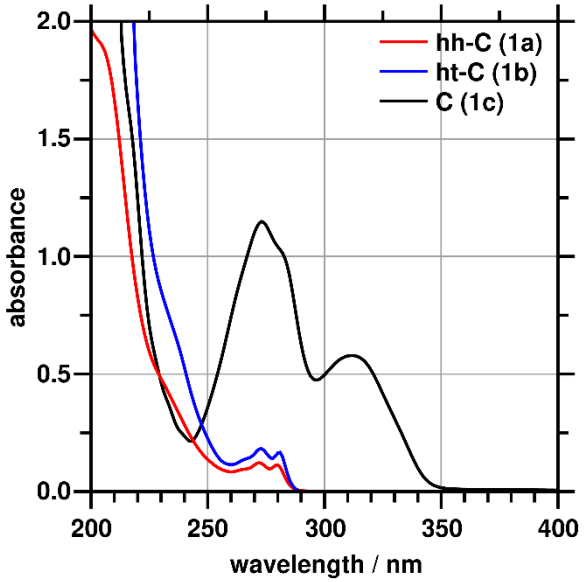

Figure S 2: UV/Vis spectra of C (**1c**) and the corresponding dimers (c = 0.1 mM in acetonitrile).

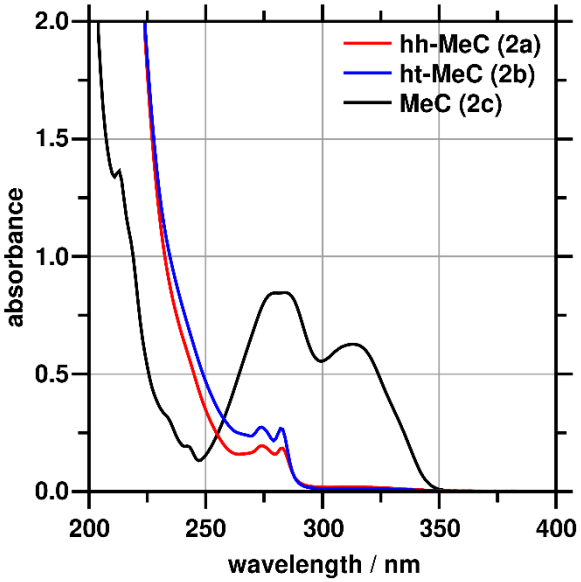

Figure S 3: UV/Vis spectra of MeC (**2c**) and the corresponding dimers (c = 0.1 mM in acetonitrile).

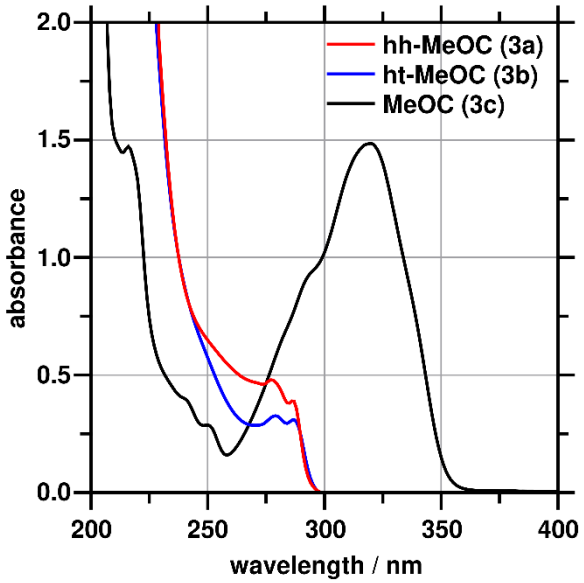

Figure S 4: UV/Vis-spectra of MeOC (**3c**) and the corresponding dimers (c = 0.1 mM in acetonitrile).

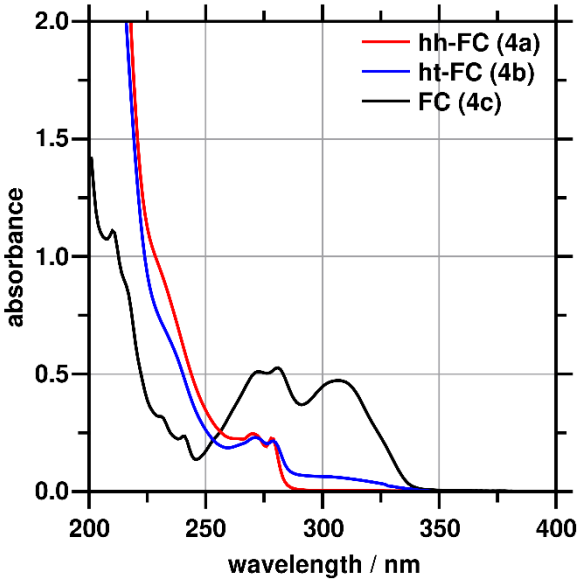

Figure S 5: UV/Vis-spectra of FC (**4c**) and the corresponding dimers (c = 0.1 mM in acetonitrile).

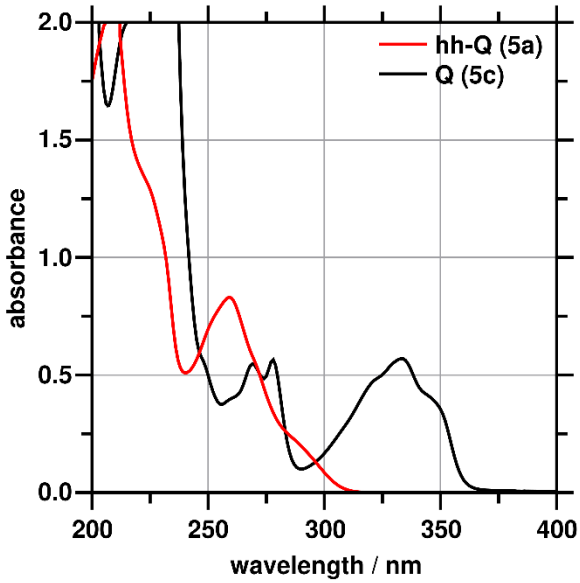

Figure S 6: UV/Vis-spectra of Q (**5c**) and the corresponding dimer (c = 0.1 mM in acetonitrile).

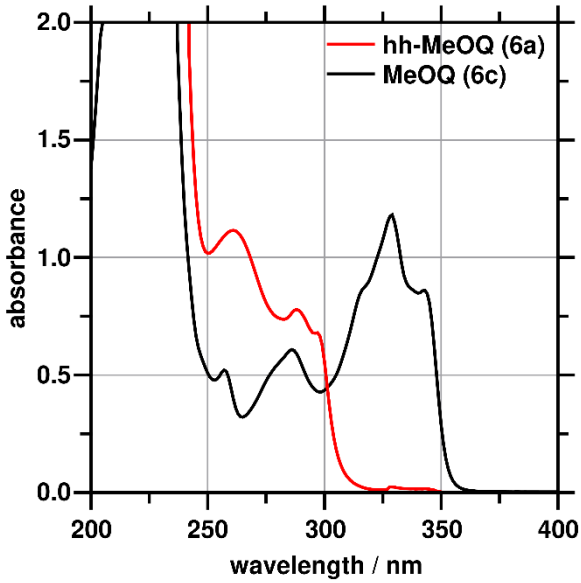

Figure S 7: UV/Vis-spectra of MeOQ (**6c**) and the corresponding dimer (c = 0.1 mM in acetonitrile).

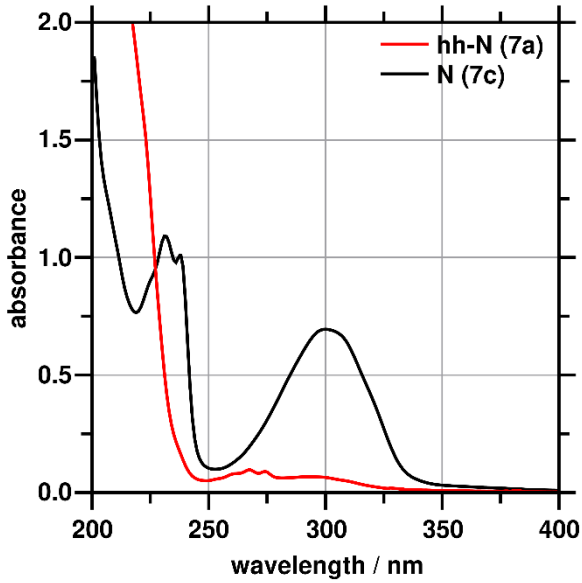

Figure S 8: UV/Vis-spectra of N (**7c**) and the corresponding dimer (c = 0.1 mM in acetonitrile).

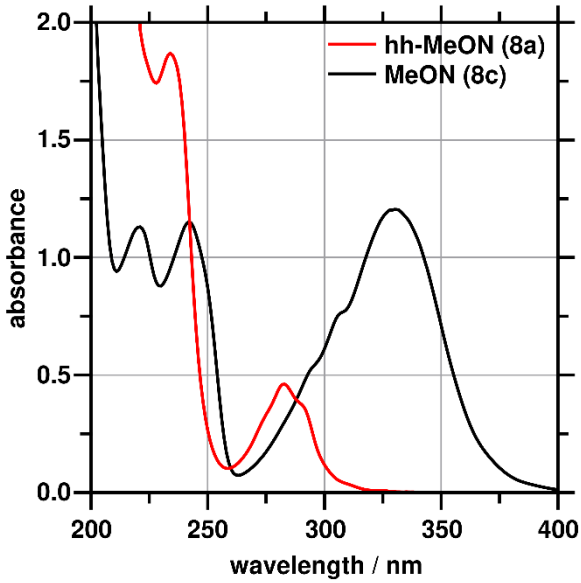

Figure S 9: UV/Vis spectra of MeON (**8c**) and the corresponding dimer (c = 0.1 mM in acetonitrile).

3 HPLC-data before and after long-term irradiation of the dimers in a Rayonet batch reactor

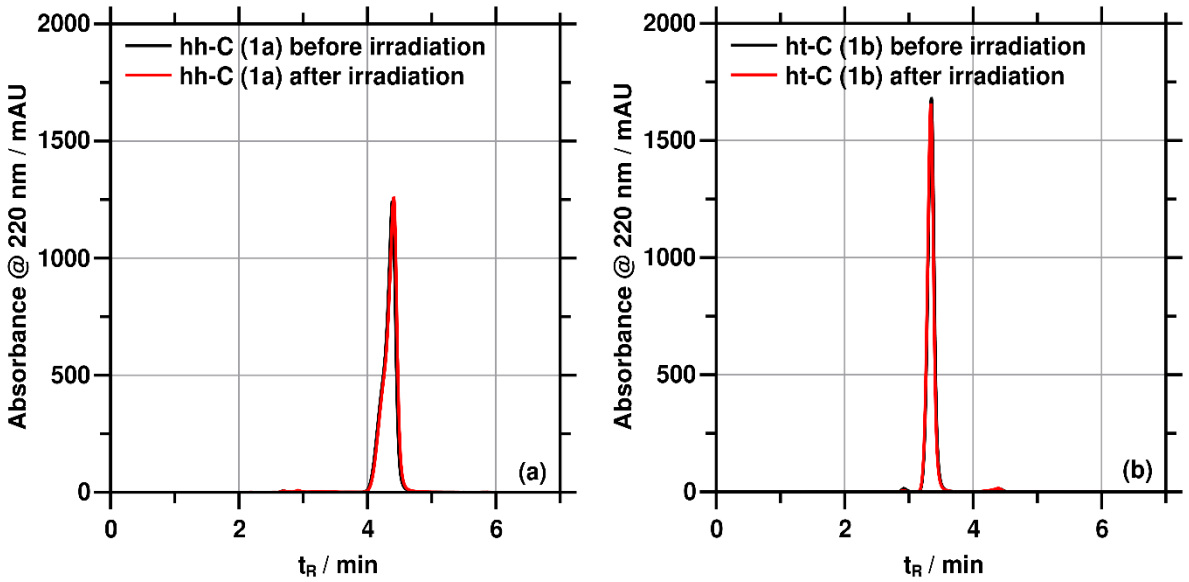

Figure S 10: Chromatogramms before and after 24 hours of irradiation in the Rayonet-type batch reactor for the dimers hh-C (**1a**, left) and ht-C (**1b**, right).

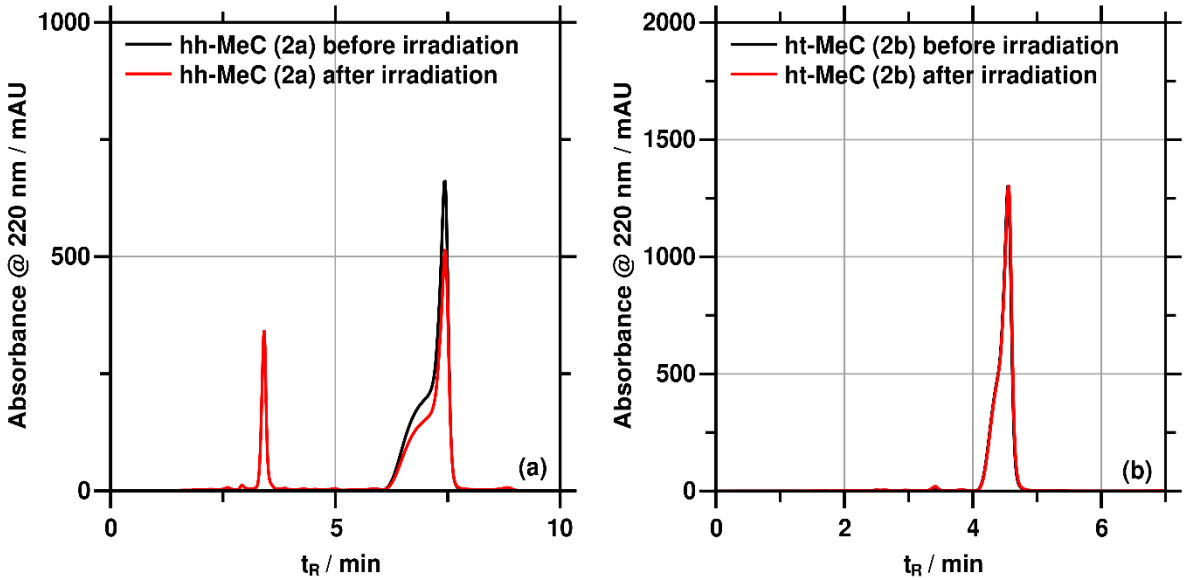

Figure S 11: Chromatogramms before and after 24 hours of irradiation in the Rayonet-type batch reactor for the dimers hh-MeC (**2a**, left) and ht-MeC (**2b**, right).

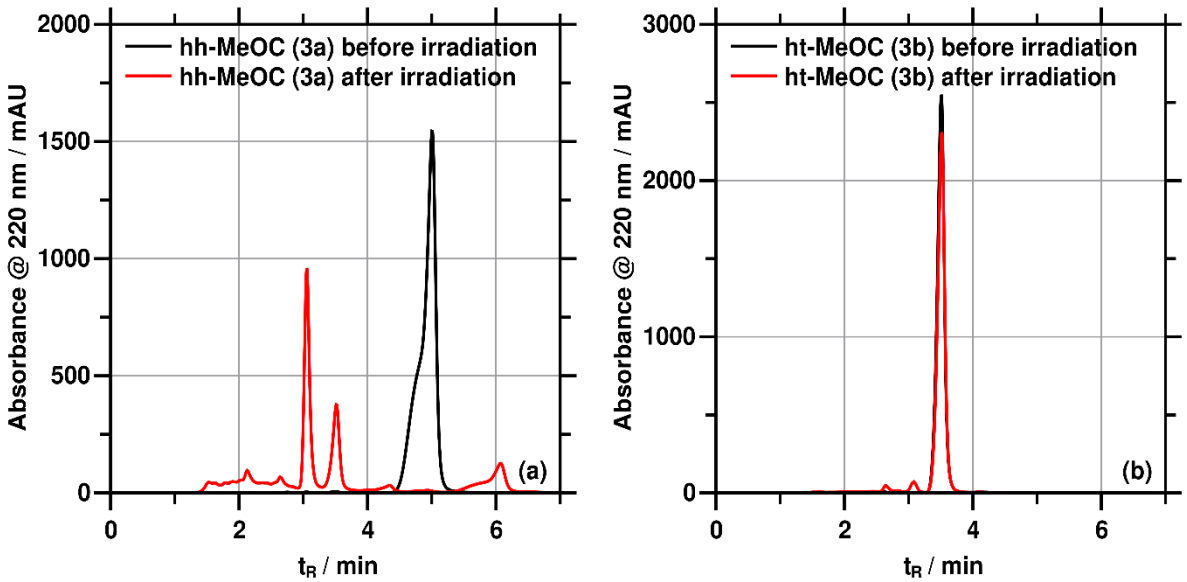

Figure S 12: Chromatogramms before and after 24 hours of irradiation in the Rayonet-type batch reactor for the dimers hh-MeOC (**3a**, left) and ht-MeOC (**3b**, right).

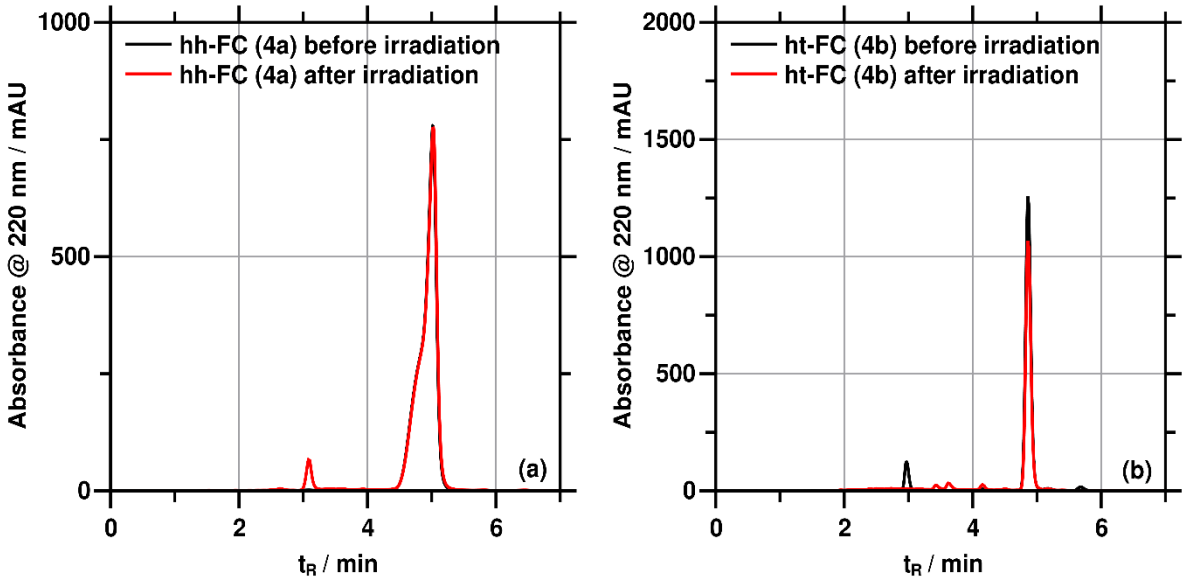

Figure S 13: Chromatogramms before and after 24 hours of irradiation in the Rayonet-type batch reactor for the dimers hh-FC (**4a**, left) and ht-FC (**4b**, right).

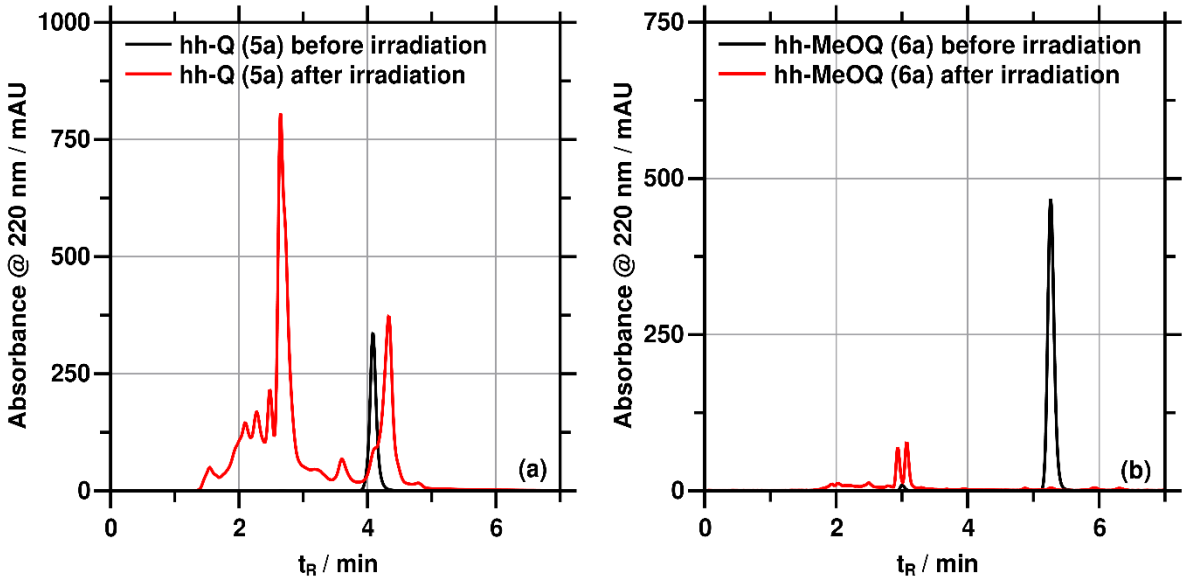

Figure S 14: Chromatogramms before and after 24 hours of irradiation in the Rayonet-type batch reactor for the dimers hh-Q (**5a**, left) and hh-MeOQ (**6a**, right).

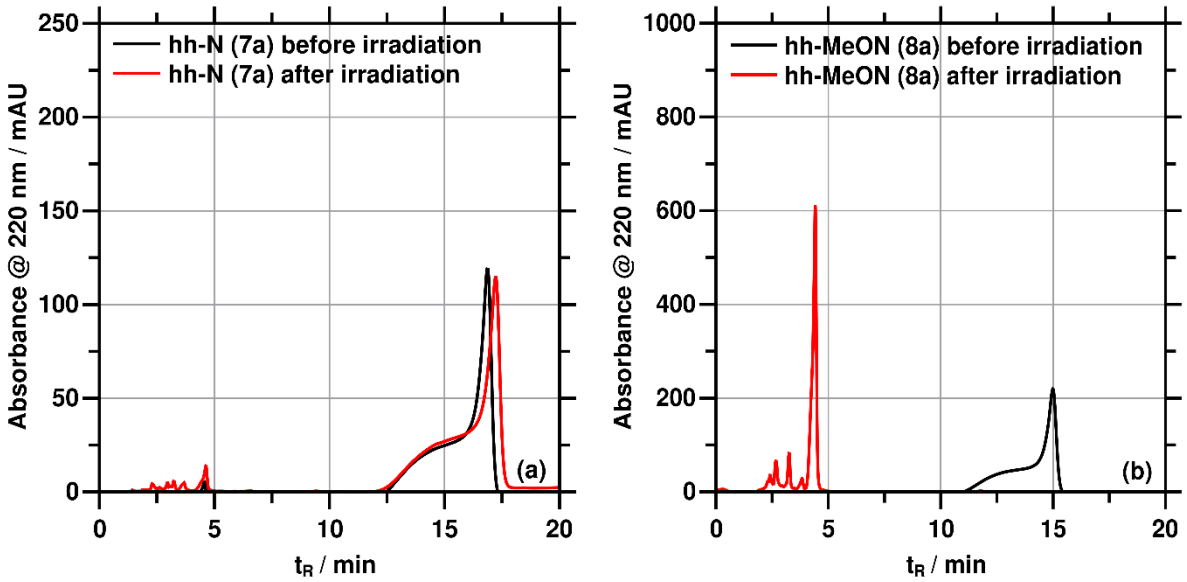

Figure S 15: Chromatogramms before and after 24 hours of irradiation in the Rayonet-type batch reactor for the dimers hh-N (**7a**, left) and hh-MeON (**7a**, right).

4 Determination of the quantum yield for SPA-induced cyclobutane cleavage at 265 nm

Solutions containing 0.1 mM of the corresponding dimer in acetonitrile (HPLC-grade) were irradiated by a mounted UV-LED with a core-wavelength of 265 nm. The reaction progress was followed via UV/Vis-spectroscopy. The dimer concentration was intentionally chosen that low as the cyclobutane cleavage via SPA-induced absorption follows zeroth order kinetics, thus we can exclude influences of oxygen on the reaction, as this would be of higher kinetic order. Once the photon is absorbed, the cleavage takes place on a femtosecond timescale, the collision with dissolved oxygen can therefore be neglected within this short lifetime of the excited states and the given concentration.[S3] The quantum yield of the reaction was determined by only considering the slope of the initial conversions to exclude effects as back dimerization from the monomeric species or other side reactions. The obtained results are in favour with previously reported values. The quantum yield calculation may here be presented for the dimer hh-Q (**5a**):

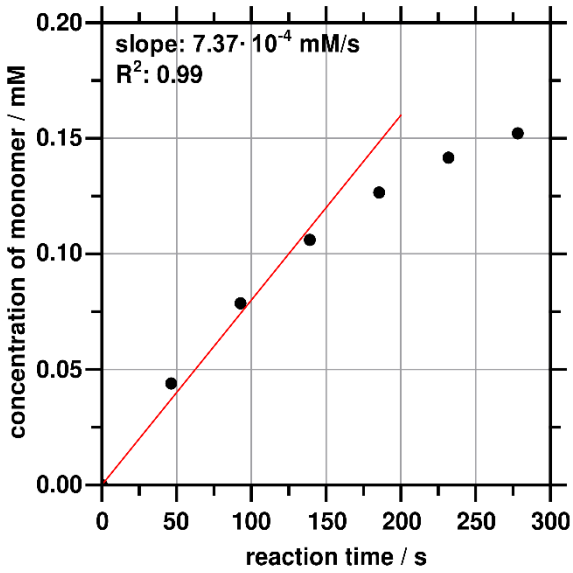

Figure S 16: Determination of the initial rate constant of dimer cleavage presented for hh-Q (**5a**).

The rate constant of the reaction was determined by assuming a linear relationship between conversion and time at the beginning (Figure S 16). The value obtained was $k_{Clea} = 7.37 \cdot 10^{-4}$ mM/s. Considering that two monomeric units result from the cleavage of one dimer molecule, the reactions volume (2 mL) and AVOGADRO's number, the number of cleaved dimers was calculated as $N_{Clea} = 4.44 \cdot 10^{14}$ 1/s. The number of photons penetrating the reaction cell was determined previously via actinometry utilizing the *cis/trans*-isomerization of azobenzene as $N_{Photon} = 1.87 \cdot 10^{15}$ 1/s. As the reactions were carried out at low concentrations, this value has to be corrected by means of transmission at the excitation wavelength. In case of hh-Q (**5a**), the optical density of the solution at 265 nm is $OD_{265\ nm} = 1.58$, thus approximately 2.6 % of the light

is not absorbed. The number of photons absorbed is then calculated as $N_{Photon,corr.}$ = 1.82·10^{15} 1/s. This given, the quantum yield can be determined as:

$$\Phi_{SPA} = \frac{N_{Clea}}{N_{Photon,corr.}} = 0.24$$

5 Control experiments regarding cyclobutane cleavage by singlet oxygen

Control experiments regarding the influence of singlet oxygen on the cleavage of the cyclobutane dimers were performed. We limited our investigations on the dimers hh-MeOC (**3a**), hh-Q (**5a**) and hh-MeON (**8a**) as these show the highest conversion upon long-time irradiation in the Rayonet-type batch reactor.

In a first experiment, 2 mL of an air-saturated solution containing 10 mM of dimer and 0.15 eq of Eosin Y (sodium salt) in acetonitrile and water (5 % *v/v*) were irradiated by a LED-array (24 W, 536 nm) for twelve hours. Eosin Y is known to be a sensitizer for singlet oxygen upon irradiation with green light, which is utilized in several organic reactions.[S7–S9] The reaction progress was monitored by HPLC, the chromatograms for the three investigated structures after twelve hours of irradiation are given in Figures S 17-19:

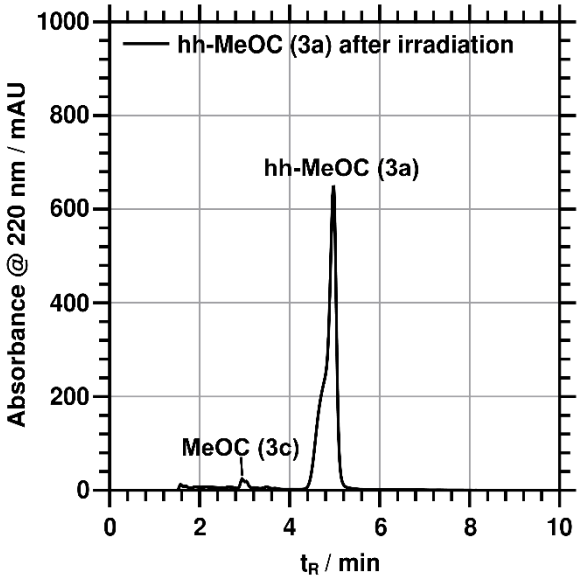

Figure S 17: Chromatogram of the sample containing hh-MeOC (**3a**) and Eosin Y after twelve hours of irradiation with 536 nm.

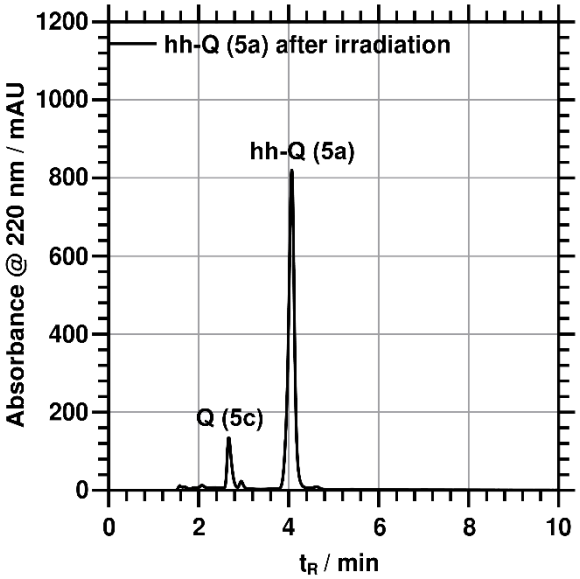

Figure S 18: Chromatogram of the sample containing hh-Q (5**a**) and Eosin Y after twelve hours of irradiation with 536 nm.

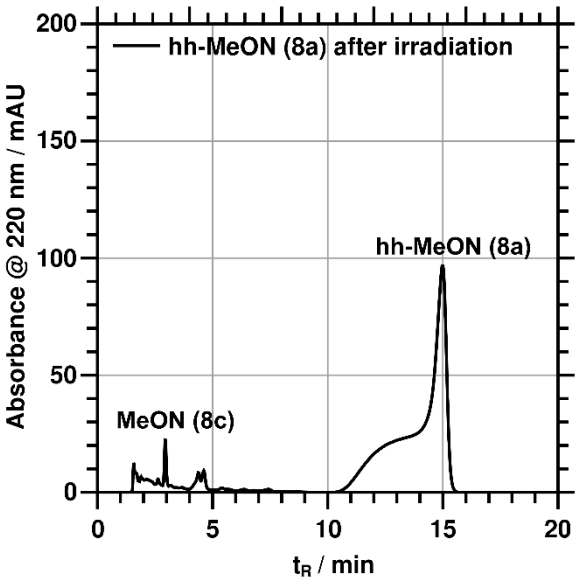

Figure S 19: Chromatogram of the sample containing hh-MeON (**8a**) and Eosin Y after twelve hours of irradiation with 536 nm.

Irradiation of hh-MeOC (**3a**) led to a yield of 5 % from dimer to monomer. For hh-Q (**5a**) we achieved 11 % and for hh-MeON (**8a**) 10 % conversion. These rather low values might result from the quenching of singlet oxygen by water, which we had to add to obtain a full solubility of Eosin Y. As the coumarin dimers are known to form their lactone open derivatives in nucleophilic solvents, we were not able to perform the experiments in methanol which might result in a higher degree of conversion and a better solubility of the photocatalyst. However, for hh-Q (**5a**) we obtained a yield of approximately 20 % in methanol, as the quinolinone framework is inert against nucleophilic attacks. The results are in favour with our proposed mechanism of singlet-oxygen induced cyclobutane cleavage.

Furthermore, we performed experiments that aim towards the suppression of singlet oxygen. The reactions were carried out under the same conditions as the experiments towards cyclobutane cleavage upon long-term irradiation with UV-A light given in the manuscript. 2 mL of a 10 mM solutions containing hh-MeOC (**3a**) or hh-MeON (**8a**) and sodium azide, which is known to be a potent singlet oxygen quencher, were irradiated for 24 hours in the Rayonet-type batch reactor. The chromatograms of the samples after irradiation are shown in Figures S 20 and S 21. Without sodium azide, the dimers hh-MeOC (**3a**) and hh-MeON (**8a**) were completely consumed after the long-term irradiation (see Figure S 12a and S 15 b). Addition of the singlet oxygen quencher leads to a decreased conversion of only 14 % for hh-MeOC (**3a**) and 20 % for hh-MeON (**8a**). A study on the influence of singlet oxygen on the dimer cleavage in hh-Q (**5a**) was published recently.[S10] As well as the experiments with Eosin Y as a singlet-oxygen sensitizer, these experiments carried

out with a singlet-oxygen quencher demonstrate the influence of the highly reactive oxygen species on cyclobutane cleavage.

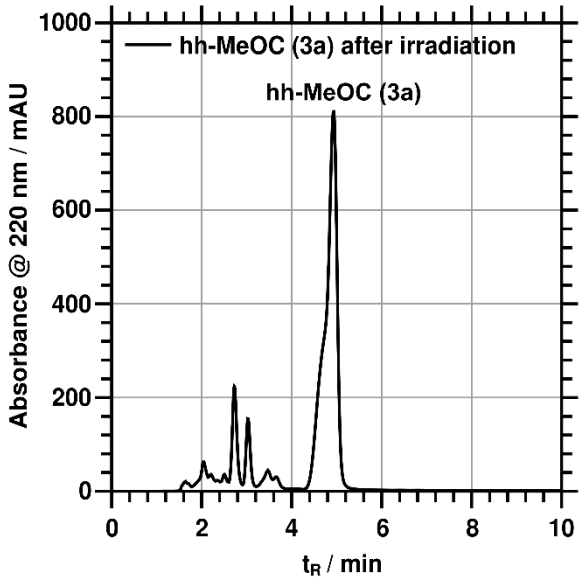

Figure S 20: Chromatogram of the sample containing hh-MeOC (**3a**) and sodium azide after 24 hours of irradiation in the Rayonet-type batch reactor.

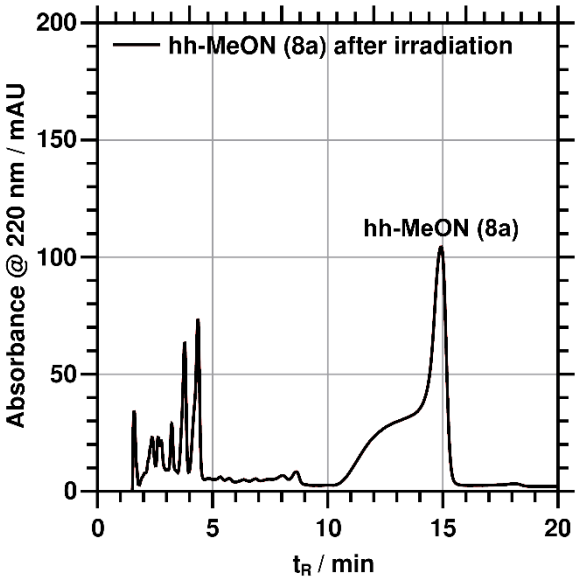

Figure S 21: Chromatogram of the sample containing hh-MeOC (**3a**) and sodium azide after 24 hours of irradiation in the Rayonet-type batch reactor.

The last line in our argumentation towards cyclobutane cleavage initiated by singlet-oxygen is given by the preparative dimerization-reactions that were performed to obtain the investigated dimers. These reactions were carried out in the Rayonet-type batch reactor under inert conditions for several days and can therefore be taken as references for long-term irradiations under inert atmosphere. If the observed dimer cleavage would be initiated just by absorption, the synthesis of e.g. hh-MeOC (**3a**) would not be possible as this species would cleave back into the monomer and form the inert ht-MeOC (**3b**). In fact, we observed nearly full conversions for all the investigated structures from monomer to dimer under inert conditions with a good selectivity of isomers formed.

6 Absorption coefficients at 320 nm and torsion angles of the investigated dimers

Table S1: Absorption coefficients of the monomers at 320 nm in acetonitrile.

	$\epsilon_{320\,\mathrm{nm}}^{ACN}$ $[\frac{\mathrm{L}}{\mathrm{mol \cdot cm}}]$
C (**1**)	4,294
MC (**2**)	5,818
MOC (**3**)	13,452
FC (**4**)	3,086
Q (**5**)	5,028
MOQ (**6**)	9,786
N (**7**)	5,601
MON (**8**)	8,320

Table S2: Cyclobutane torsion angles of dimers

	head-to-head	head-to-tail
C (**1**)	19.9	10.7
MC (**2**)	19.8	10.4
MOC (**3**)	23.9	3.9
FC (**4**)	7.9	12.0
Q (**5**)	23.9	
MOQ (**6**)	23.8	
N (**7**)	24.8	
MON (**8**)	5.8	

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