

Supporting Information

Wavelength-Dependent Photochemistry of Oxime Ester Photoinitiators

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1. Experimental

Materials. Irgacure® OXE01 and OXE02 were kindly provided by BASF and used as received. Methyl methacrylate (MMA, Sigma-Aldrich, 99 %, stabilized) was freed from inhibitor by passing through a column of activated basic alumina (Sigma-Aldrich). Tetrahydrofuran (THF, VWR, HPLC grade) for the SEC measurements was employed as received.

Polymerizations with LEDs. Polymerization samples were prepared with a photoinitiator concentration of $c_{PI} = 1 \cdot 10^{-3}$ or $5 \cdot 10^{-3}$ mol·L⁻¹ in methyl methacrylate (0.5 mL) and freed from oxygen by purging with nitrogen. Polymerizations were conducted with LEDs as light sources ($\lambda = 385, 400, 420, 435$ and 450 nm) for 1 hour. After polymerization, the remaining monomer was evaporated and the conversion was determined by gravimetry (average of 3 measurements per irradiation wavelength). The forward currents of the LEDs were adjusted, according to the specification sheets, to yield a photon flux of $4.27 \cdot 10^{16}$ s⁻¹ at every wavelength.

Size Exclusion Chromatography (SEC). SEC measurements were performed on a PL-SEC 50 Plus Integrated System, comprising an autosampler and a PLgel 5 μ m bead-size guard column (50×7.5 mm) followed by a PLgel 5 μ m Mixed E column (300×7.5 mm), three PLgel 5 μ m Mixed C columns (300×7.5 mm), and a differential refractive index (RI) detector using THF as eluent at 35 °C with a flow rate of 1 mL·min⁻¹. The SEC system is calibrated using linear poly(methyl methacrylate) standards ranging from 800 to $1.6 \cdot 10^6$ g·mol⁻¹. SEC calibration was carried out relative to poly(methyl methacrylate) calibrations (Mark Houwink parameters $K = 12.8 \cdot 10^{-5}$ dL·g⁻¹; $\alpha = 0.68$).

UV-vis spectroscopy. UV-vis spectra of **OXE01** and **OXE02** were recorded on a Shimadzu UV-2102 PC UV-vis scanning spectrophotometer in acetonitrile. LED emission spectra were recorded on a J&M Tidas (J&M, Aalen, Germany) fiber-optics, diode array spectrometer.

2. DFT

OXE01. The S_1 singlet excitation has $n-\pi^*$ character and occurs mainly from the HOMO-6 (localized at the lone pairs of the benzoyl group oxygen and of the nitrogen atom) into the LUMO (localized at the π -system of the benzoyloxy moiety plus large contributions at C-N). The S_2 singlet excitation has $\pi-\pi^*$ character and occurs mainly from the HOMO (localized at the π -system of the diphenyl sulphide moiety including the sulfur lone pair) into the LUMO. The first six vertical singlet excitations are listed in Table S1 and the corresponding molecular orbitals (MOs) are depicted in Figure S1.

Table S1. Vertical Singlet Excitations of OXE01, as Computed by the CAM-B3LYP/6-311++G(2d,p) Method in Acetonitrile

OXE01	S1	S2	S3	S4	S5	S6
eV	3.7735	3.969	4.5931	4.8807	4.961	5.0147
nm	328.6	312.4	269.9	254.0	249.	247.2
f	0.0119	0.6301	0.0033	0.0011	0.0336	0.0975
M01	112 \rightarrow 119	118 \rightarrow 119	113 \rightarrow 119	118 \rightarrow 121	115 \rightarrow 120	115 \rightarrow 120
c	0.62	0.65	0.42	0.65	0.40	0.34
M02	108 \rightarrow 119		116 \rightarrow 119		115 \rightarrow 119	108 \rightarrow 119
c	0.16		0.36		0.31	0.27
M03			118 \rightarrow 122		108 \rightarrow 119	114 \rightarrow 119
c			0.22		-0.22	0.22
M04					111 \rightarrow 119	111 \rightarrow 119
c					0.20	-0.22
M05						114 \rightarrow 120
c						0.19

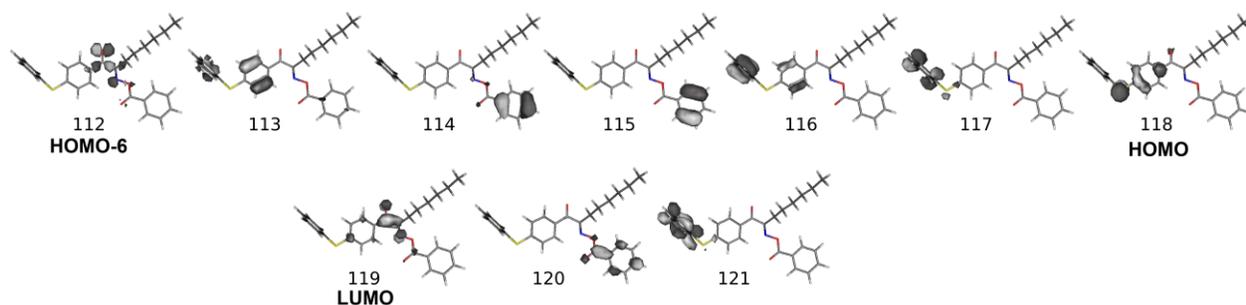


Figure S1. Molecular orbitals of **OXE01** in the S_0 singlet ground state; contour values of 0.05 a.u. were applied.

OXE02. The S_1 and S_2 singlet excitations have mixed $n-\pi^*/\pi-\pi^*$ character and occur mainly from the HOMO-5 (localized at the oxygen lone pairs of the benzoyl group) and the HOMO (localized at the ethyl-carbazole moiety) into the LUMO (localized at the π -system of the benzoyl moiety with large contributions at the carbonyl group). The S_3 singlet excitation occurs mainly from the HOMO into the LUMO+1. The first six vertical singlet excitations are listed in Table S2 and the corresponding molecular orbitals (MOs) are depicted in Figure S2.

Table S2. Vertical Singlet Excitations of OXE02, as Computed by the CAM-B3LYP/6-311++G(2d,p) Method in Acetonitrile

OXE02	S1	S2	S3	S4	S5	S6
eV	3.9548	4.0463	4.1575	4.5258	4.6802	4.8395
nm	313.5	306.4	298.2	274.0	264.9	256.2
f	0.1792	0.2018	0.1878	1.0306	0.2047	0.1157
M01	109 \rightarrow 110	109 \rightarrow 110	109 \rightarrow 111	108 \rightarrow 110	109 \rightarrow 112	107 \rightarrow 110
c	0.42	0.37	0.46	0.44	0.51	0.42
M02	104 \rightarrow 110	104 \rightarrow 110	108 \rightarrow 110	108 \rightarrow 111	109 \rightarrow 111	108 \rightarrow 111
c	-0.40	0.37	-0.30	-0.37	-0.31	0.39
M03	106 \rightarrow 110	109 \rightarrow 112	109 \rightarrow 110	109 \rightarrow 111	105 \rightarrow 110	108 \rightarrow 110
c	0.21	-0.26	0.26	0.29	0.20	0.17
M04		106 \rightarrow 110	108 \rightarrow 112		109 \rightarrow 110	
c		-0.19	0.19		0.17	
M05		108 \rightarrow 110	109 \rightarrow 112			
c		0.17	0.17			

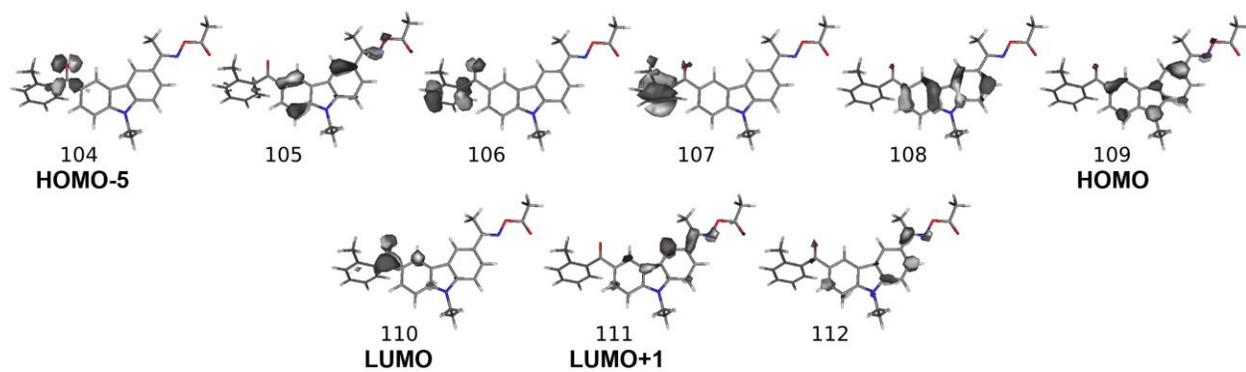


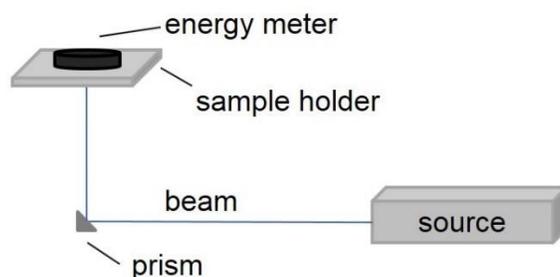
Figure S2. Molecular orbitals of **OXE02** in the S_0 singlet ground state; contour values of 0.05 a.u. were applied.

3. Wavelength-Variable PLP-SEC-ESI-MS

Tunable UV laser light was generated by an Innolas Tunable Laser System SpitLight 600 OPO. An optical parametric oscillator (OPO) was pumped with a diode pumped Nd:YAG laser (repetition rate 100 Hz). The energy output of the laser was regulated by an attenuator (polarizer).

As shown in Scheme S1, the laser beam is redirected by a prism and enters the sample in a custom-made sample holder from below. The sample holder consists of a metal block with a vertical cylindrical hole (0.71 cm diameter), which can hold the vials used for the experiments. These 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).

Scheme S1. Experimental Setup for the Measurement of the Laser Energy



Calibration Procedure for Constant Photon Count. The transmittance of the glass vials that were used for photoreactions with the tunable laser system was determined experimentally using the tunable laser setup. 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 top part of the glass vial was removed for these measurements (Figure S3). Thus, only the absorbance of the bottom of the vial is detected. The described procedure was performed for three individual glass vials to account for variability between the vials and the obtained averaged values are listed in Table S3.



Figure S3. Left: vial after removal of the top part; right: crimped vial.

Table S3. Transmittance of Glass Vials

λ / nm	mean transmittance / %	mean deviation / %
270	0	0
275	0	0
280	0	0
285	13.4	0.2
290	19.7	0.6
295	30.3	0.5
300	37.7	1.0
305	45.6	0.5
310	47.5	1.0
315	51.1	0.6
320	56.3	1.2
325	58.9	0.8
330	61.0	0.9
335	62.9	0.9
340	60.4	0.9
345	64.5	1.6
350	60.4	1.1
355	62.1	0.9
360	65.1	0.3
370	65.9	1.2
380	66.3	1.2
390	70.8	0.4
400	66.9	0.9
410	68.0	1.9
430	75.3	0.6
450	76.6	0.8
470	77.6	0.5
490	79.1	0.5

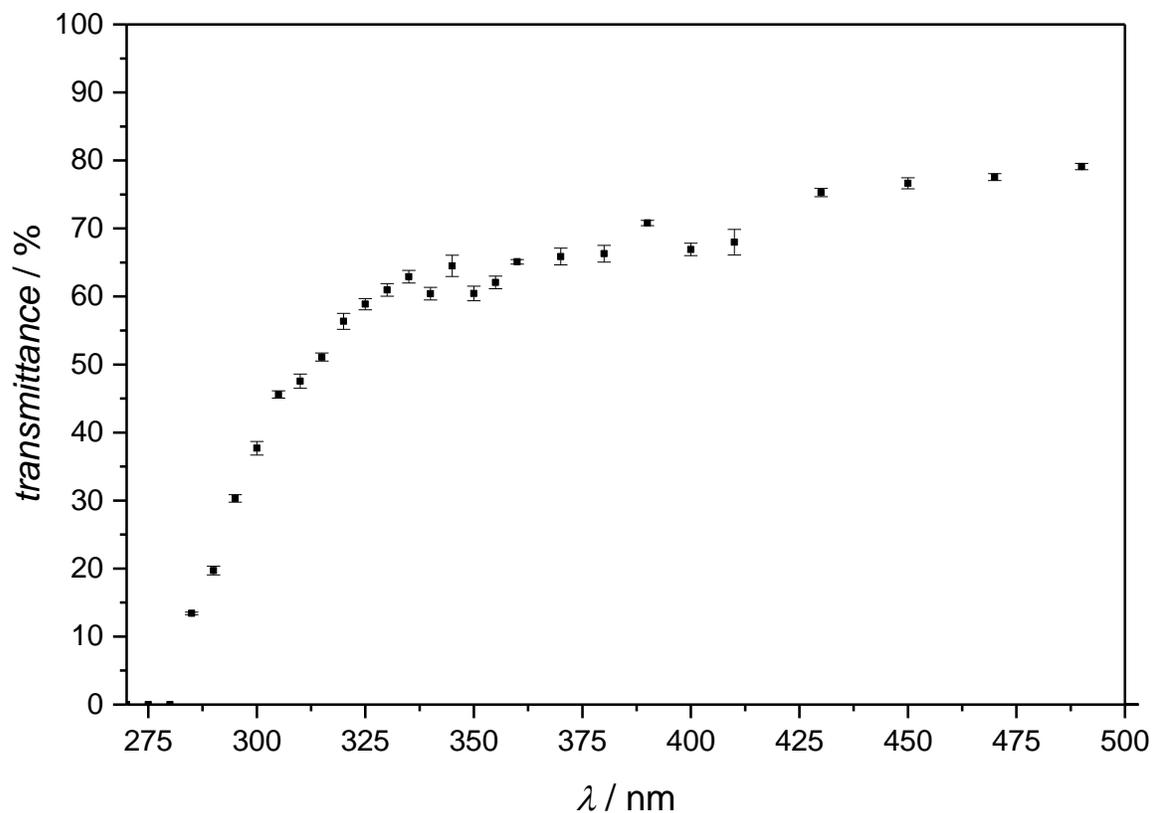


Figure S4. Transmittance of glass vials dependent on irradiation wavelength.

For all irradiation wavelengths a ‘target energy’ was calculated. The target energy per pulse (E^0) was defined as the measured energy in case of an empty sample holder. For each irradiation experiment the attenuator position, defined and controlled by the measurement of E^0 , enables irradiation of each sample solution with a defined number of photons. The target energy per pulse E^0 was calculated according to eq. S1 with 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_{hv} .

$$E^0 = \frac{n_{hv} \cdot h \cdot c}{k \cdot T_\lambda \cdot \lambda} \quad (\text{eq. S1})$$

Thus, the number of photons penetrating each sample solution is equal.

Table S4. Irradiation Parameters and Conversion of MMA Initiated by OXE01

Sample	Irradiation wavelength λ / nm	Target energy per pulse E / μ J	Number of pulses n_p / a.u.	Number of incident photons n_{ph} / μ mol	Conversion p / %	Mean conversion p / %	Mean deviation d / %
1	285	700	270000	60	3.415	3.28	0.123
2	285	700	270000	60	3.237		
3	285	700	270000	60	3.178		
4	300	709	90000	60	2.172	2.21	0.095
5	300	709	90000	60	2.319		
6	300	709	90000	60	2.140		
7	315	498	90000	60	2.494	2.51	0.025
8	315	498	90000	60	2.494		
9	315	498	90000	60	2.537		
10	330	398	90000	60	1.570	2.71	0.075
11	330	398	90000	60	2.791		
12	330	398	90000	60	2.649		
13	345	371	90000	60	2.154	2.26	0.271
14	345	371	90000	60	2.052		
15	345	371	90000	60	2.565		
16	360	334	90000	60	3.060	3.044	0.436
17	360	334	90000	60	2.600		
18	360	334	90000	60	3.471		
19	375	328	90000	60	5.131	4.76	0.326
20	375	328	90000	60	4.539		
21	375	328	90000	60	4.599		
22	390	305	90000	60	7.464	6.63	0.258
23	390	305	90000	60	7.628		
24	390	305	90000	60	6.933		
25	405	286	90000	60	9.533	9.37	0.173
26	405	286	90000	60	9.401		
27	405	286	90000	60	9.190		
28	420	260	90000	60	8.836	8.70	0.127
29	420	260	90000	60	8.673		
30	420	260	90000	60	8.587		
31	435	244	90000	60	2.993	2.90	0.116
32	435	244	90000	60	2.938		
33	435	244	90000	60	2.770		

Table S5. Irradiation Parameters and Conversion of MMA Initiated by OXE02

Sample	Irradiation wavelength λ / nm	Target energy per pulse E / μ J	Number of pulses n_p / a.u.	Number of incident photons n_{ph} / μ mol	Conversion p / %	Mean conversion p / %	Mean deviation d / %
1	285	700	270000	60	0.776	0.90	0.107
2	285	700	270000	60	0.984		
3	285	700	270000	60	0.920		
4	300	709	90000	60	0.669	0.50	0.149
5	300	709	90000	60	0.389		
6	300	709	90000	60	0.442		
7	315	498	90000	60	0.847	0.88	0.026
8	315	498	90000	60	0.886		
9	315	498	90000	60	0.895		
10	330	398	90000	60	0.869	1.035	0.148
11	330	398	90000	60	1.151		
12	330	398	90000	60	1.086		
13	345	371	90000	60	0.737	0.84	0.112
14	345	371	90000	60	0.812		
15	345	371	90000	60	0.958		
16	360	334	90000	60	1.911	1.70	0.190
17	360	334	90000	60	1.666		
18	360	334	90000	60	1.536		
19	375	328	90000	60	1.658	1.66	0.122
20	375	328	90000	60	1.782		
21	375	328	90000	60	1.538		
22	390	305	90000	60	2.278	2.16	0.099
23	390	305	90000	60	2.110		
24	390	305	90000	60	2.101		
25	405	286	90000	60	3.072	3.07	0.116
26	405	286	90000	60	2.948		
27	405	286	90000	60	3.179		
28	420	260	90000	60	1.079	0.99	0.164
29	420	260	90000	60	1.099		
30	420	260	90000	60	0.806		
31	435	244	90000	60	0.900	0.96	0.104
32	435	244	90000	60	1.078		
33	435	244	90000	60	0.894		

Table S6. Overview of the Wavelength-Dependent Conversion of MMA Initiated by OXE01 and OXE02, Synthesized by PLP with a Constant Photon Count (60 μmol) per Irradiation Wavelength, and the Corresponding Molar Extinction Coefficients (ϵ)

λ / nm	OXE01		OXE02	
	<i>conversion of MMA / %</i>	$\epsilon / \text{L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$	<i>conversion of MMA / %</i>	$\epsilon / \text{L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$
435	2.9 ± 0.2	0.4 ± 0.1	1.0 ± 0.2	0.3 ± 0.1
420	8.7 ± 0.2	4.5 ± 0.1	1.0 ± 0.2	0.7 ± 0.1
405	9.4 ± 0.2	45 ± 1	3.1 ± 0.2	2.2 ± 0.1
390	6.6 ± 0.3	310 ± 5	2.2 ± 0.1	29 ± 1
375	4.8 ± 0.4	1400 ± 50	1.7 ± 0.2	630 ± 10
360	3.0 ± 0.5	4600 ± 100	1.7 ± 0.2	6200 ± 50
345	2.3 ± 0.3	11000 ± 150	0.8 ± 0.2	17500 ± 100
330	2.7 ± 0.1	17300 ± 250	1.0 ± 0.2	18700 ± 150
315	2.5 ± 0.1	14000 ± 300	0.9 ± 0.1	13100 ± 150
300	2.2 ± 0.1	7600 ± 400	0.5 ± 0.2	35400 ± 300
285	3.3 ± 0.2	5000 ± 600	0.9 ± 0.2	32100 ± 450

High resolution SEC-ESI-MS spectra of OXE01-initiated pMMA synthesized by variable-wavelength PLP @ 285, 315, 345, 375, 405 and 435 nm

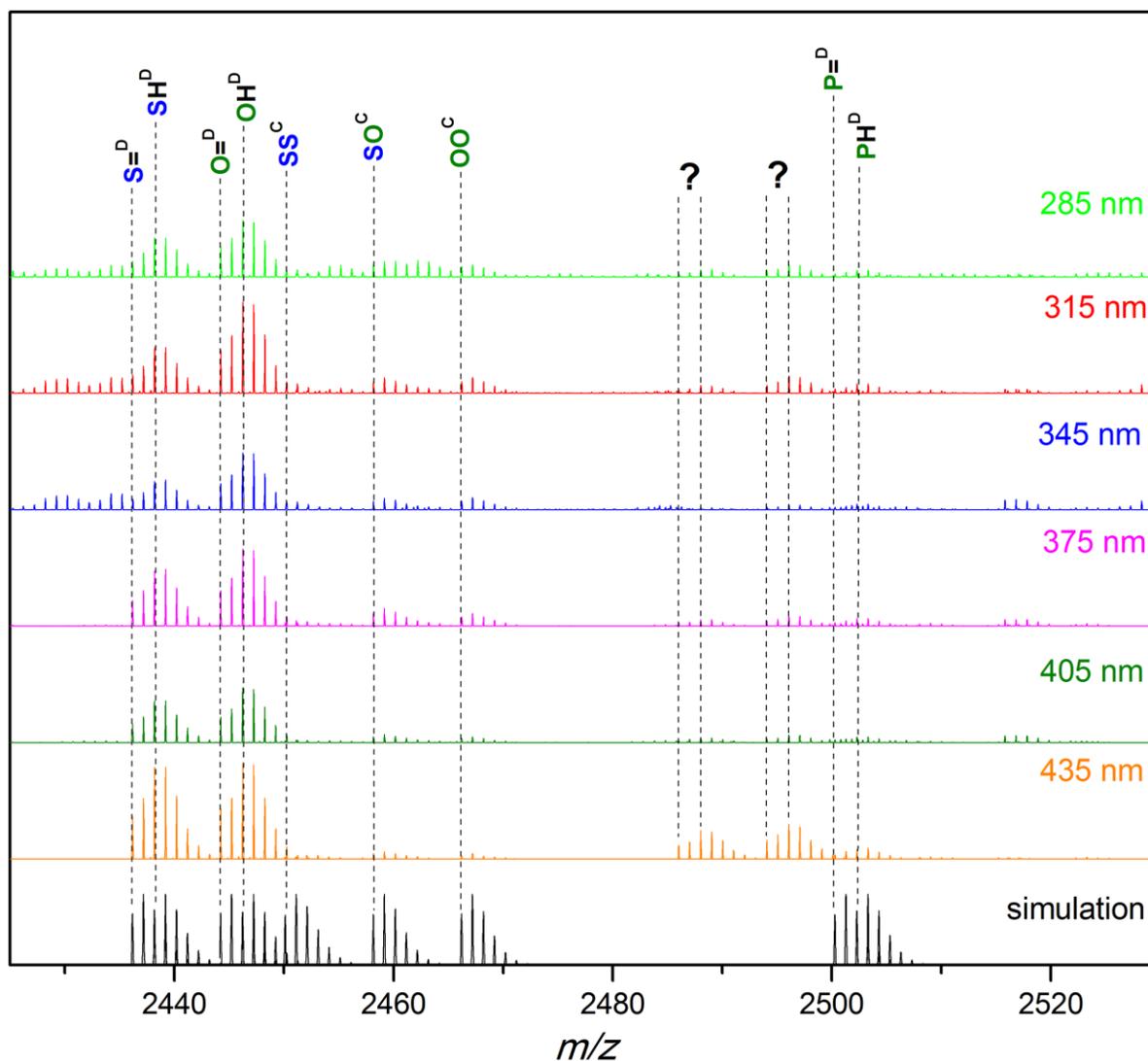
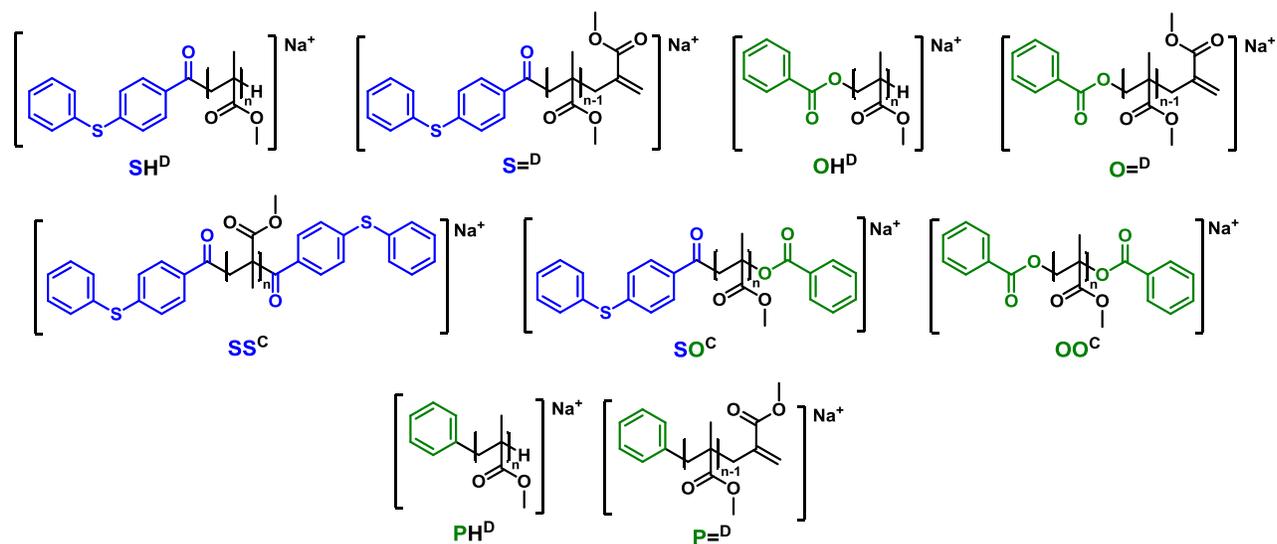


Figure S5. High resolution SEC-ESI-MS spectra of **OXE01**-initiated pMMA synthesized by variable-wavelength PLP (285 nm – 435 nm, 100 Hz, 18 °C) at a constant photon count and the theoretical isotope patterns (signals marked with ? have not been assigned a polymer structure yet).

Scheme S2. Overview of the Assigned Polymer Products of OXE01-Initiated PMMA Synthesized by Variable-Wavelength PLP (285 nm – 435 nm, 100 Hz, 18 °C) at a Constant Photon Count, as Detected by High Resolution SEC-ESI-MS (R = 42100 - 43100)



High resolution SEC-ESI-MS spectra of OXE02-initiated pMMA synthesized by variable-wavelength PLP @ 285, 315, 345, 375 and 405 nm

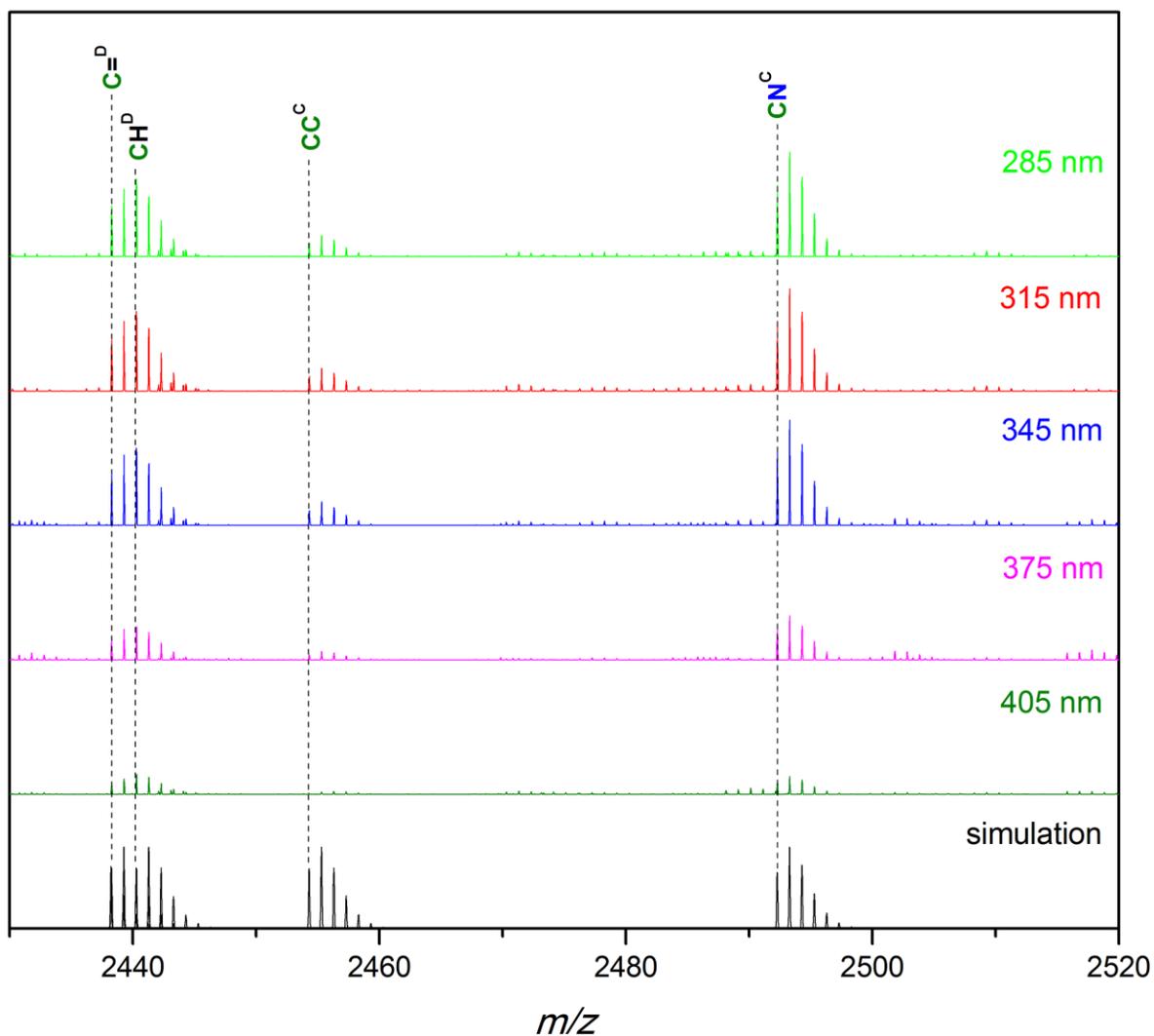
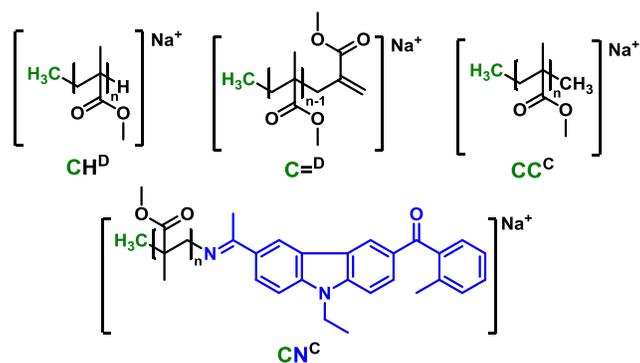


Figure S6. High resolution SEC-ESI-MS spectra of **OXE02**-initiated pMMA synthesized by variable-wavelength PLP (285 nm – 435 nm, 100 Hz, 18 °C) at a constant photon count and the theoretical isotope patterns.

Scheme S3. Overview of the Assigned Polymer Products of OXE02-Initiated PMMA Synthesized by Variable-Wavelength PLP (285 nm – 405 nm, 100 Hz, 18 °C) at a Constant Photon Count, as Detected by High Resolution SEC-ESI-MS (R = 42100 - 43100)



4. Polymerizations with LEDs

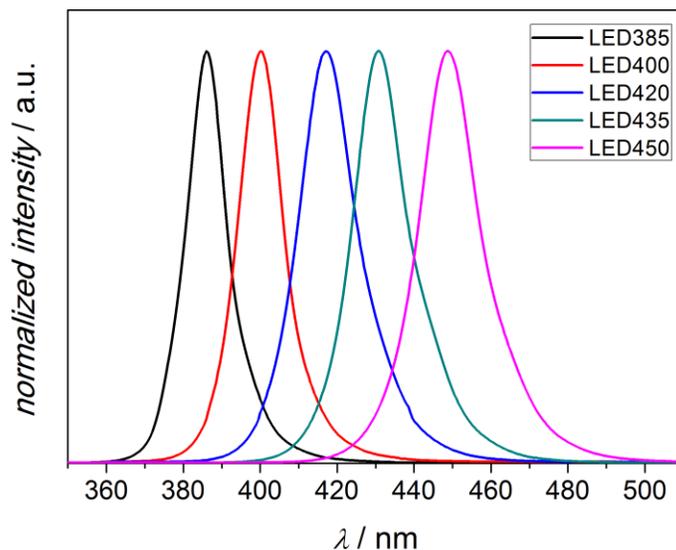


Figure S7. Emission spectra of the LEDs ($\lambda = 385, 400, 420, 435$ and 450 nm).

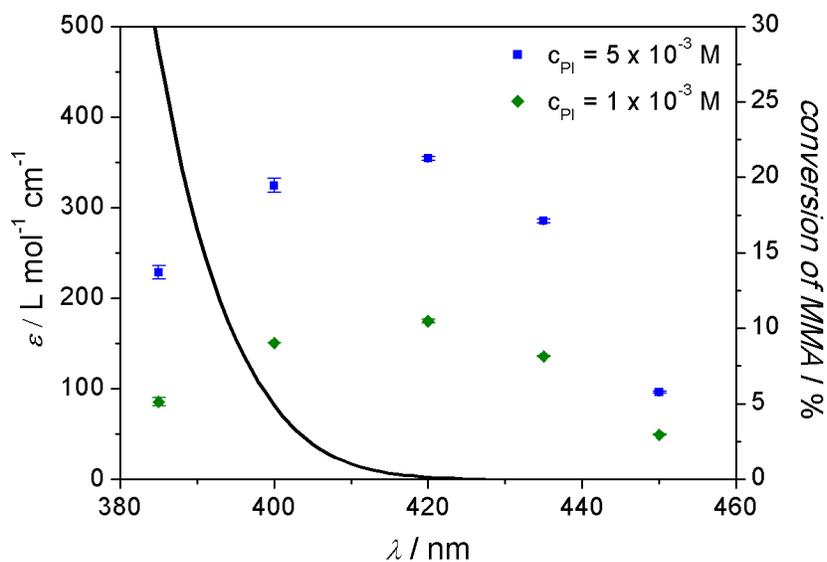


Figure S8. Comparison of the UV-vis spectrum of **OXE01** ($c_{\text{PI}} = 5 \cdot 10^{-3} \text{ M}$ in acetonitrile) and the wavelength-dependent conversion of methyl methacrylate initiated by **OXE01** ($c_{\text{PI}} = 5 \cdot 10^{-3} \text{ M}$, blue; $c_{\text{PI}} = 10^{-3} \text{ M}$, green), synthesized under LED irradiation (1 hour).

Table S7. Wavelength-Dependent Conversion of MMA Initiated by OXE01 ($c_{PI} = 10^{-3}$ and $5 \cdot 10^{-3}$ M) Synthesized Under LED Irradiation, and the Corresponding Molar Extinction Coefficients ϵ

$c_{PI} =$	$5 \cdot 10^{-3}$ M	10^{-3} M	
λ / nm	<i>conversion of MMA / %</i>		$\epsilon / \text{L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$
450	5.8 ± 0.1	3.0 ± 0.1	0.04 ± 0.01
435	17.1 ± 0.2	8.2 ± 0.1	0.37 ± 0.03
420	21.3 ± 0.2	10.5 ± 0.2	4.5 ± 0.1
400	19.5 ± 0.5	9.0 ± 0.1	87 ± 2
385	13.7 ± 0.5	5.1 ± 0.3	530 ± 10

Table S8. Number and Weight Average Molecular Weights (M_n and M_w) and Dispersities \mathcal{D} of MMA Initiated by OXE01 ($c_{PI} = 5 \cdot 10^{-3}$ M) Synthesized Under LED Irradiation

λ / nm	$M_n / \text{g} \cdot \text{mol}^{-1}$	$M_w / \text{g} \cdot \text{mol}^{-1}$	\mathcal{D}
450	144000	337000	2.3
435	44500	93900	2.1
420	29500	71400	2.4
400	21700	74300	3.4
385	14700	150700	10.3

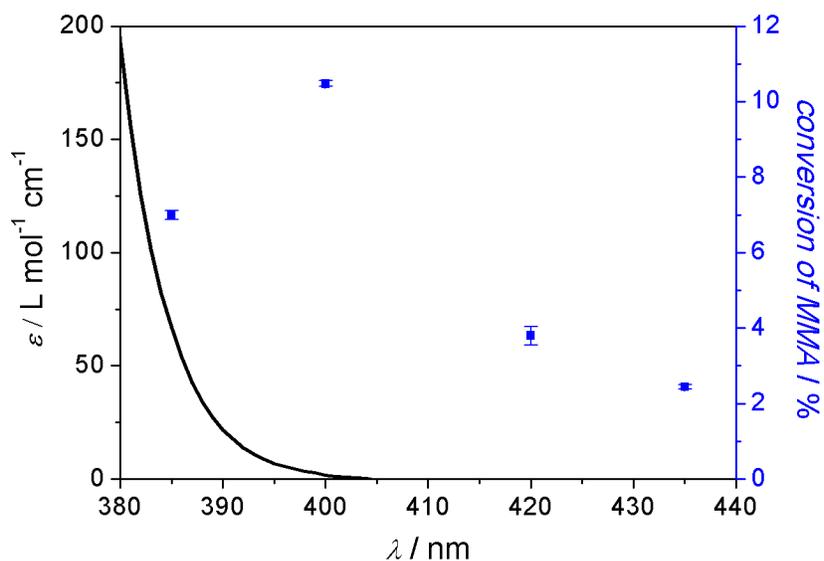


Figure S9. Comparison of the UV-vis spectrum of **OXE02** ($c_{PI} = 5 \cdot 10^{-3}$ M in acetonitrile) and the wavelength-dependent conversion of methyl methacrylate initiated by **OXE02** ($c_{PI} = 5 \cdot 10^{-3}$ M), synthesized under LED irradiation (1 hour).

Table S9. Wavelength-Dependent Conversion of MMA Initiated by OXE02 ($c_{PI} = 5 \cdot 10^{-3}$ M) Synthesized Under LED Irradiation, and the Corresponding Molar Extinction Coefficients

ϵ

λ / nm	conversion of MMA / %	$\epsilon / \text{L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$
435	2.4 ± 0.1	0.31 ± 0.02
420	3.8 ± 0.3	0.66 ± 0.06
400	10.5 ± 0.1	4.8 ± 0.1
385	7.0 ± 0.2	89 ± 4

Table S10. Number and Weight Average Molecular Weights (M_n and M_w) and Dispersities \mathcal{D} of MMA Initiated by OXE02 ($c_{PI} = 5 \cdot 10^{-3}$ M) Synthesized Under LED Irradiation

λ / nm	M_n / g·mol ⁻¹	M_w / g·mol ⁻¹	\mathcal{D}
435	220000	540000	2.4
420	116000	306000	2.7
400	32000	72900	2.3
385	19400	102000	5.3

5. Calculations based on the Lambert-Beer Law

The percentage of absorbed light (*PAL*) at 2 cm under PLP conditions ($c_{\text{PI}} = 5 \cdot 10^{-3}$ M) and the path length at which 99 % of the incident light are absorbed ($l_{99\%}$) were calculated according to the Lambert-Beer law (eq. S2 – S4).

$$A_{\lambda} = \varepsilon_{\lambda} \cdot c \cdot l \quad (\text{eq. S2})$$

$$T_{\lambda} = 10^{-A_{\lambda}} \quad (\text{eq. S3})$$

$$PAL_{\lambda} = (1 - T_{\lambda}) \cdot 100 \quad (\text{eq. S4})$$

A_{λ} absorbance at wavelength λ

ε_{λ} molar extinction coefficient at wavelength λ ($\text{L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$)

c molar concentration ($\text{mol} \cdot \text{L}^{-1}$)

l path length of the light through the sample (cm)

T_{λ} transmittance at wavelength λ

PAL_{λ} percentage of absorbed light at wavelength λ

Table S11. Molar Extinction Coefficients (ε) and Calculated Values of the Percentage of Absorbed Light (*PAL*) at 2 cm and the Path Length at which 99 % of the Incident Light are Absorbed ($l_{99\%}$) Based on the Lambert-Beer Law for OXE01

λ / nm	$\varepsilon / \text{L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$	<i>PAL</i> at 2 cm / %	$l_{99\%} / \text{cm}$
435	0.37 ± 0.03	0.9 ± 0.1	1100 ± 100
420	4.5 ± 0.1	9.8 ± 0.3	90 ± 5
405	45 ± 1	65 ± 1	9 ± 0.5
394	200 ± 10	99 ± 0.2	2.0 ± 0.1

Table S12. Molar Extinction Coefficients (ϵ) and Calculated Values of the Percentage of Absorbed Light (*PAL*) at 2 cm and the Path Length at which 99 % of the Incident Light are Absorbed ($l_{99\%}$) Based on the Lambert-Beer Law for OXE02

λ / nm	ϵ / L·mol ⁻¹ ·cm ⁻¹	<i>PAL</i> at 2 cm / %	$l_{99\%}$ / cm
435	0.31 ± 0.02	0.7 ± 0.1	1300 ± 100
420	0.66 ± 0.06	1.5 ± 0.2	610 ± 60
405	2.2 ± 0.1	5.0 ± 0.3	180 ± 10
390	29 ± 1	50 ± 2	14 ± 0.5
381	195 ± 5	99 ± 0.2	2.1 ± 0.1