Supporting Information

Intensification of Heterogeneous Photocatalytic Reactions using Wireless Light Emitters: The Case Study of Nitrobenzene Reduction

Hong T. Duong,[1] Bruno Ortner,[2] Alexander Sutor,[2] Bastien O. Burek,[1] Jonathan Z. Bloh[1]

[1] DECHEMA-Forschungsinstitut, Theodor-Heuss-Allee 25, 60486 Frankfurt am Main, Germany, jonathan.bloh@dechema.de

[2] UMIT TIROL, Eduard-Wallnöfer-Zentrum 1, 6060 Hall in Tirol, Austria

1. Actinometry

1.1. External illumination

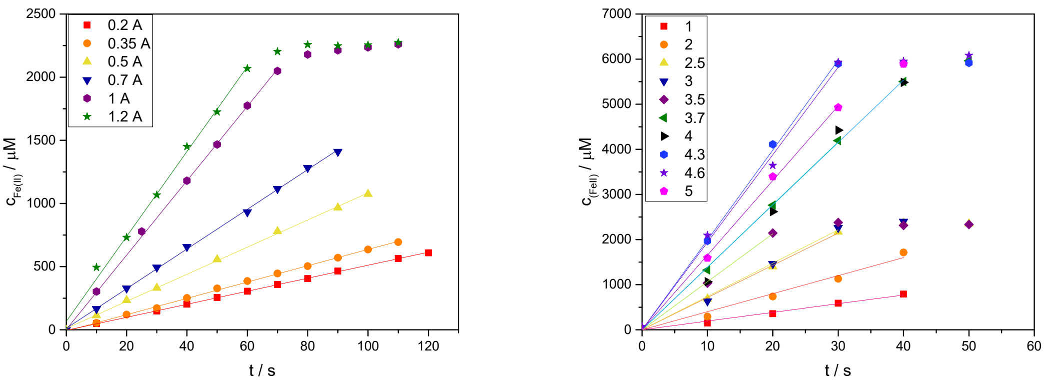

Figure S1.: Concentration-time-profiles of the iron(II) generation under illumination of the ferrioxalate solution. Reaction conditions: 50 mL ferrioxalate solution. Left: M365LP1. Right: SOLIS-365C.

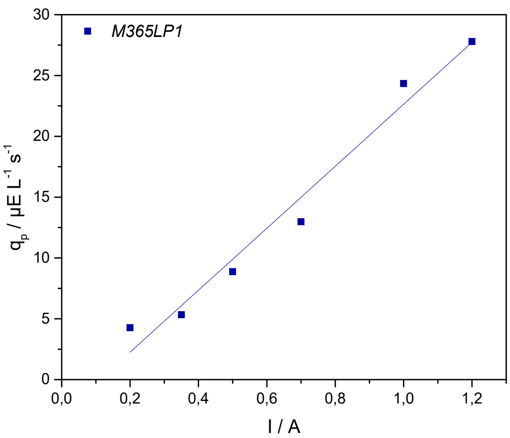

Figure S2.: Photon flux density (q_p) in dependence of LED driver current of the external illumination systems (M365LP1).

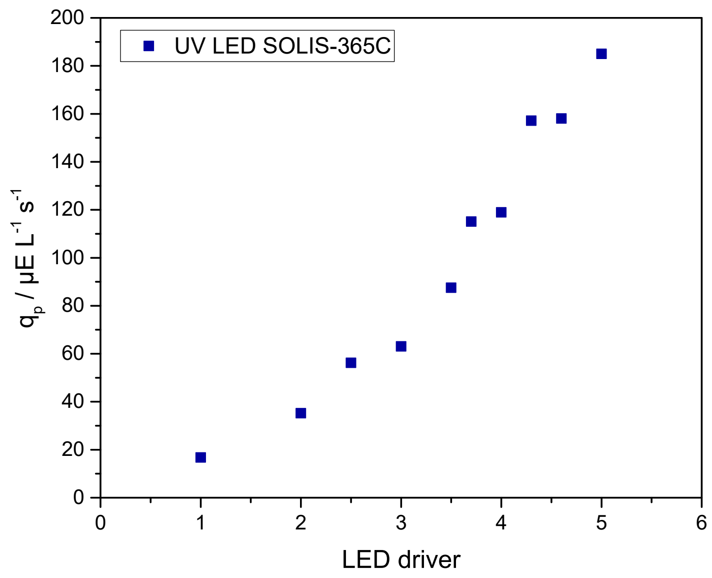

Figure S3.: The determined photon flux densitiy q_p of the external irradiation setup (SOLIS-365C) against the predefined LED driver settings.

Table S1.: The determined photon flux density q_p, light power density P_{light}, total light power P_{light}, power consumption P_{el} and wall plug efficiency WPE of the external irradiation system (M365LP1) in a reaction volume of 50 mL.

LED driver predefined settings	q_p / µM/s	P_{light} / W/L	P_{light} / W	P_{el} / W	WPE / %
0.2	4.26	1.40	0.07	1.10	6.35
0.35	5.34	1.75	0.09	1.30	6.73
0.5	8.87	2.91	0.15	2.00	7.27
0.7	12.98	4.25	0.21	3.60	5.91
1.0	24.33	7.98	0.40	5.90	6.76
1.2	27.79	9.11	0.46	6.40	7.12

Table S2.: The determined photon flux density q_p, light power density P_{light}, total light power P_{light}, power consumption P_{el} and wall plug efficiency WPE of the external irradiation system (SOLIS-365C) in a reaction volume of 50 mL.

LED driver predefined settings	q_p / µM/s	P_{light} / W/L	P_{light} / W	P_{el} / W	WPE / %
1.0	16.76	5.49	0.27	3	9.16
2.0	35.19	11.53	0.58	5	10.68
2.5	56.24	18.43	0.92	7	12.80
3.0	63.06	20.67	1.03	9	11.61
3.5	87.53	28.69	1.43	12	12.16
3.7	115.07	37.71	1.89	14	13.57
4.0	118.93	38.98	1.95	17	11.46
4.3	157.17	51.51	2.58	22	11.60
4.6	158.05	51.80	2.59	24	10.70
5.0	184.97	60.62	3.03	24	12.53

1.2. Internal illumination: Amplifier: EAP-00

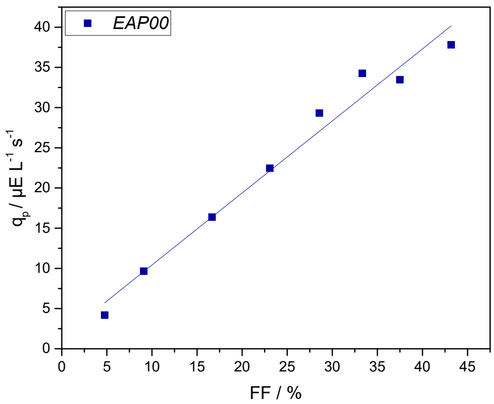

Figure S4.: Photon flux density (q_p) in dependence of the fill factor (FF) for the internal irradiation (EAP-00, 100 W)).

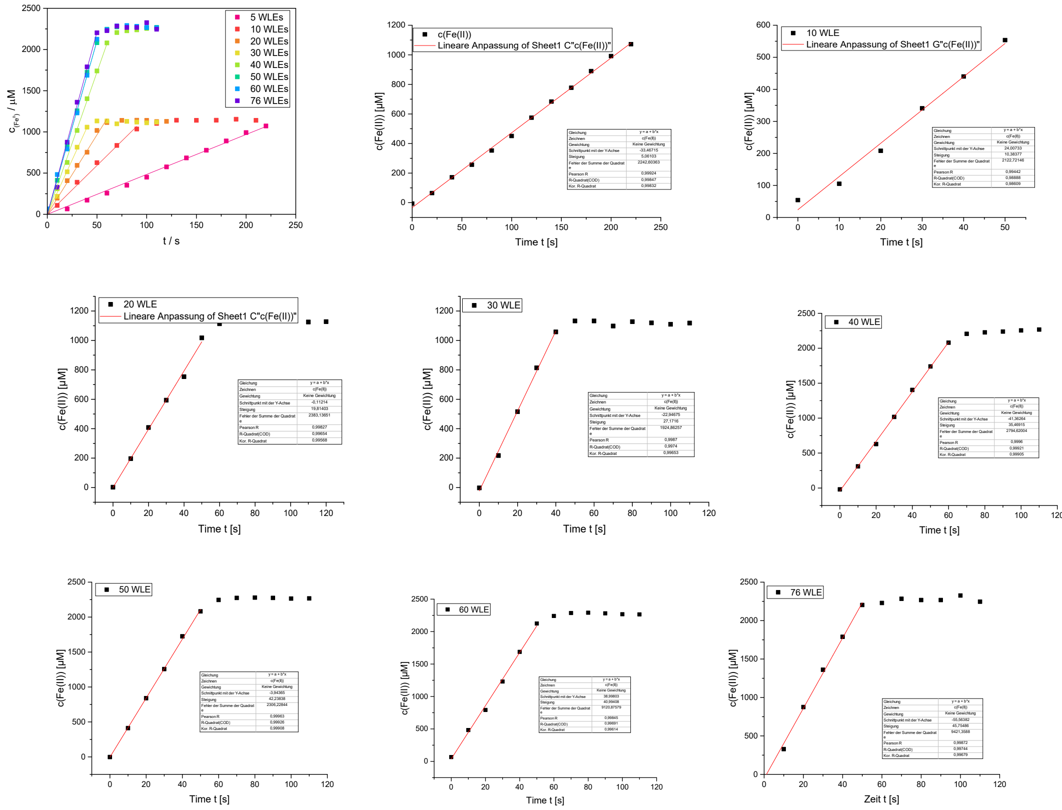

Figure S5.: Concentration-time-profiles of the iron(II) generation under illumination of the ferrioxalate solution. Reaction conditions: 50 mL ferrioxalate solution. Internal illumination: Amplifier EAP-00, 100 W. WLE number was varied between 5 to 76.

Table S3.: The determined photon flux density q_p, light power density P_{light}, total light power P_{light}, power consumption P_{el} and wall plug efficiency WPE of the internal irradiation system (EAP-00, 100W) in dependence of the number of WLE at a reaction volume of 50 mL.

Number of WLE	q_p / µM/s	P_{light} / W/L	P_{light} / W	P_{el} / W	WPE / %
5	4.18	1.371	0.0685	15.6	0.44
10	9.65	3.161	0.1581	16.6	0.95
20	16.38	5.367	0.2683	17.5	1.53
30	22.46	7.360	0.3680	18.2	2.02
40	29.31	9.607	0.4804	19.3	2.49
50	34.91	11.441	0.5720	20	2.86
60	33.88	11.104	0.5552	20.8	2.67
76	37.81	12.393	0.6197	21.5	2.88

Experiments with different liquid volumes (EAP-00, 50 W)

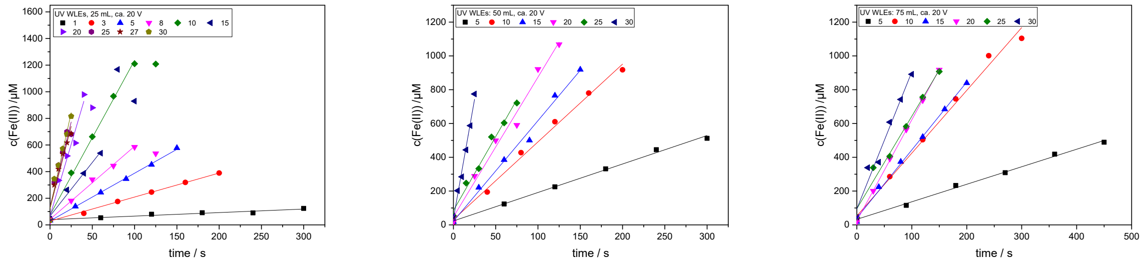

Figure S6.: Concentration-time-profiles of the iron(II) generation under illumination of the ferrioxalate solution. Different solution volume was investigated (25 mL, 50 mL and 75 mL). Different numbers of WLE (1 WLE to 30 WLE) were used for each liquid volume. Internal illumination: Amplifier EAP-00, 50 W. WLE number was varied between 1 to 30.

Table S4.: The determined photon flux density q_p, light power density P_{light}, total light power P_{light}, power consumption P_{el} and wall plug efficiency WPE of the internal irradiation system (EAP-00, 50 W) in dependence of the number of WLE at a reaction volume of 25 mL at 20 V amplifier voltage.

Number of WLE	q_p / µM/s	P_{light} / W/L	P_{light} / W	P_{el} / W	WPE / %
1	0.22	0.07	0.002	6.8	0.03
3	1.49	0.49	0.012	7	0.17
5	2.96	0.97	0.024	7.2	0.34
8	3.63	1.19	0.030	7.6	0.39
10	8.10	2.66	0.066	8	0.83
15	8.61	2.82	0.071	8.7	0.81
20	14.68	4.81	0.120	9.7	1.24
25	20.95	6.87	0.172	9.8	1.75
27	20.36	6.67	0.167	10.2	1.64
30	23.79	7.80	0.195	10.5	1.86

Table S5.: The determined photon flux density q_p, light power density P_{light}, total light power P_{light}, power consumption P_{el} and wall plug efficiency WPE of the internal irradiation system (EAP-00, 50 W) in dependence of the number of WLE at a reaction volume of 50 mL at 20 V amplifier voltage.

Number of WLE	q_p / µM/s	P_{light} / W/L	P_{light} / W	P_{el} / W	WPE / %
5	1.39	0.46	0.023	7.1	0.32
10	3.80	1.25	0.062	7.9	0.79
15	4.92	1.61	0.081	8.5	0.95
20	6.84	2.24	0.112	9.3	1.21
25	7.23	2.37	0.119	9.8	1.21
30	23.32	7.65	0.382	10.1	3.78

Table S6.: The determined photon flux density q_p, light power density P_{light}, total light power P_{light}, power consumption P_{el} and wall plug efficiency WPE of the internal irradiation system (EAP-00, 50 W) in dependence of the number of WLE at a reaction volume of 75 mL at 20 V amplifier voltage.

Number of WLE	q_p / µM/s	P_{light} / W/L	P_{light} / W	P_{el} / W	WPE / %
5	0.86	0.28	0.021	7.1	0.30
10	3.07	1.01	0.075	7.9	0.96
15	3.32	1.09	0.082	8.6	0.95
20	4.94	1.62	0.121	9.3	1.31
25	4.52	1.48	0.111	9.7	1.15
30	6.70	2.20	0.165	10.2	1.62

1.3. Internal illumination: Amplifier: EAP-01

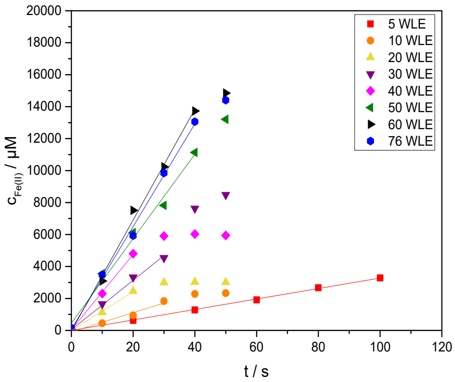

Figure S7.: Concentration-time-profiles of the iron(II) generation under illumination of the ferrioxalate solution. Reaction conditions: 50 mL ferrioxalate solution. Internal illumination: EAP-01. 320 W. WLE number was varied between 5 to 76.

1.3.1. Actinometry with 10 WLEs at different voltages (10 V to 50 V)

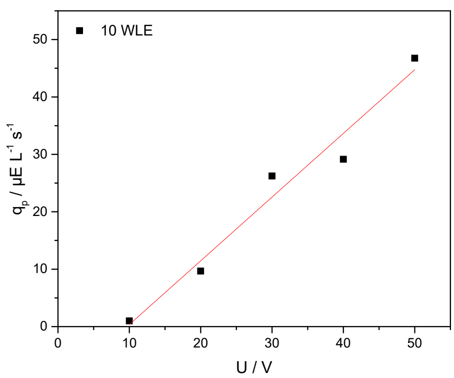

Figure S8.: Photon flux density vs. amplifier voltage curves of the iron(II) generation under illumination of the ferrioxalate solution. Reaction conditions: 50 mL ferrioxalate solution. Internal illumination with the amplifier EAP-01. 320 W. 10 WLEs. Different amplifier voltages (10 V to 50 V).

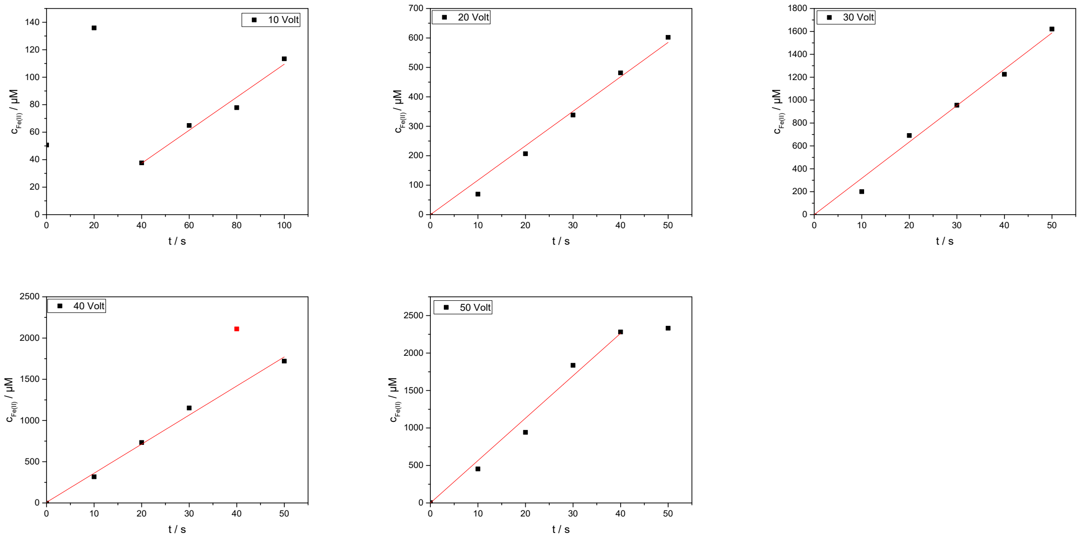

Figure S9.: Concentration-time-profiles of the iron(II) generation under illumination of the ferrioxalate solution. Reaction conditions: 50 mL ferrioxalate solution. Internal illumination with the amplifier EAP-01. 320 W. 10 WLEs. Different amplifier voltages (10 V to 50 V).

1.3.2. Actinometry with 20 WLEs at different voltages (10 V to 50 V)

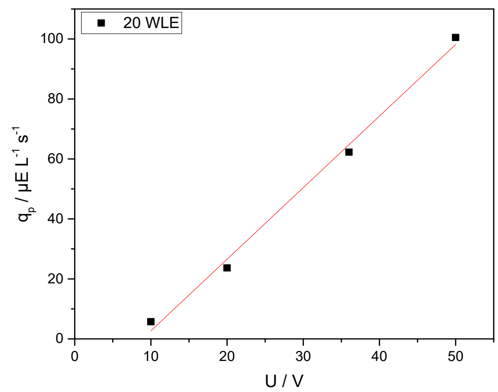

Figure S10.: Photon flux density vs. amplifier voltage curves of the iron(II) generation under illumination of the ferrioxalate solution. Reaction conditions: 50 mL ferrioxalate solution. Internal illumination with the amplifier EAP-01. 320W. 20 WLEs. Different amplifier voltages (10 V to 50 V).

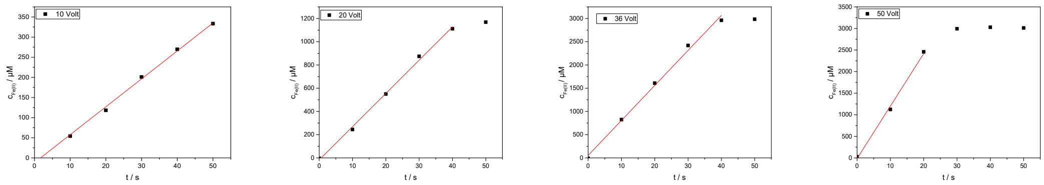

Figure S11.: Concentration-time-profiles of the iron(II) generation under illumination of the ferrioxalate solution. Reaction conditions: 50 mL ferrioxalate solution. Internal illumination with the amplifier EAP-01. 320W. 20 WLEs. Different amplifier voltages (10 V to 50 V).

1.3.3. Actinometry with 30 WLEs at 50 V

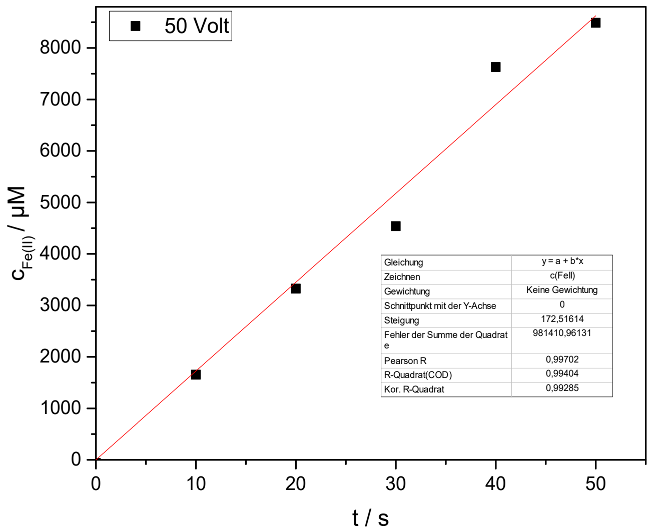

Figure S12.: Concentration-time-profile of the iron(II) generation under illumination of the ferrioxalate solution. Reaction conditions: 50 mL ferrioxalate solution. Internal illumination with the amplifier EAP-01. 320W. 30 WLEs at 50 V amplifier voltage.

1.3.4. Actinometry with 40 WLEs at different voltages (10 V to 50 V)

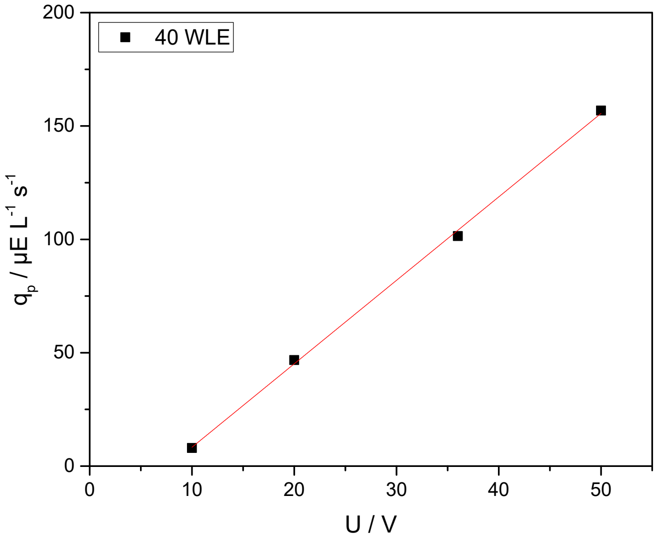

Figure S13.: Photon flux density vs. amplifier voltage curves of the iron(II) generation under illumination of the ferrioxalate solution. Reaction conditions: 50 mL ferrioxalate solution. Internal illumination with the amplifier EAP-01. 320W. 40 WLEs. Different amplifier voltages (10 V to 50 V).

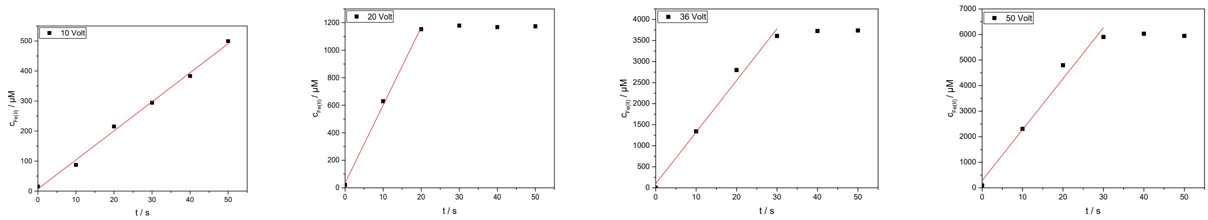

Figure S14.: Concentration-time-profiles of the iron(II) generation under illumination of the ferrioxalate solution. Reaction conditions: 50 mL ferrioxalate solution. Internal illumination with the amplifier EAP-01. 320W. 40 WLEs. Different amplifier voltages (10 V to 50 V).

1.3.5. Actinometry with 50 WLEs at 50 V

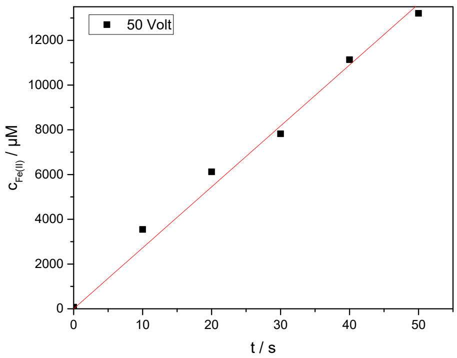

Figure S15.: Concentration-time-profile of the iron(II) generation under illumination of the ferrioxalate solution. Reaction conditions: 50 mL ferrioxalate solution. Internal illumination with the amplifier EAP-01. 320W. 50 WLEs at 50 V amplifier voltage.

1.3.6. Actinometry with 60 WLEs at different voltages (10 V to 50 V)

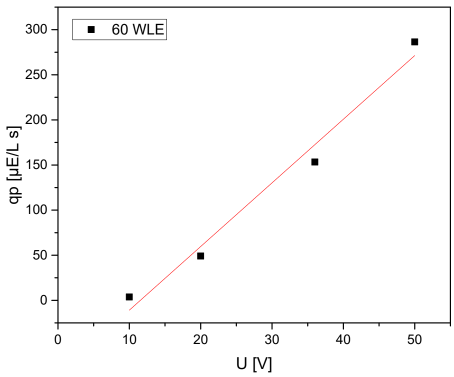

Figure S16.: Photon flux density vs. amplifier voltage curves of the iron(II) generation under illumination of the ferrioxalate solution. Reaction conditions: 50 mL ferrioxalate solution. Internal illumination with the amplifier EAP-01. 320W. 60 WLEs. Different amplifier voltages (10 V to 50 V).

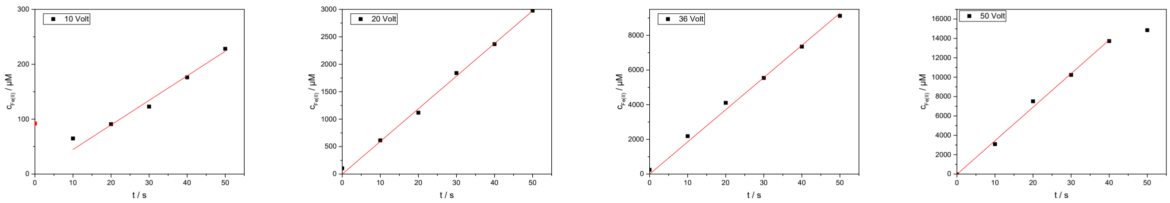

Figure S17.: Concentration-time-profiles of the iron(II) generation under illumination of the ferrioxalate solution. Reaction conditions: 50 mL ferrioxalate solution. Internal illumination with the amplifier EAP-01. 320W. 60 WLEs. Different amplifier voltages (10 V to 50 V).

1.3.7. Actinometry with 76 WLEs at different voltages (10 V to 50 V)

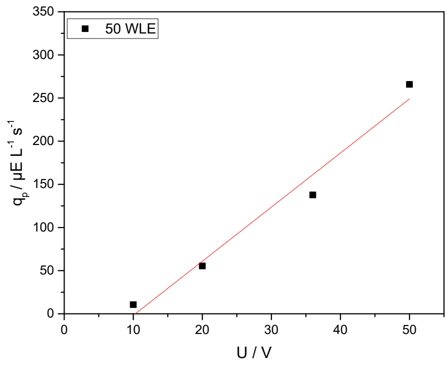

Figure S18.: Photon flux density vs. amplifier voltage curves of the iron(II) generation under illumination of the ferrioxalate solution. Reaction conditions: 50 mL ferrioxalate solution. Internal illumination with the amplifier EAP-01. 320W. 76 WLEs. Different amplifier voltages (10 V to 50 V).

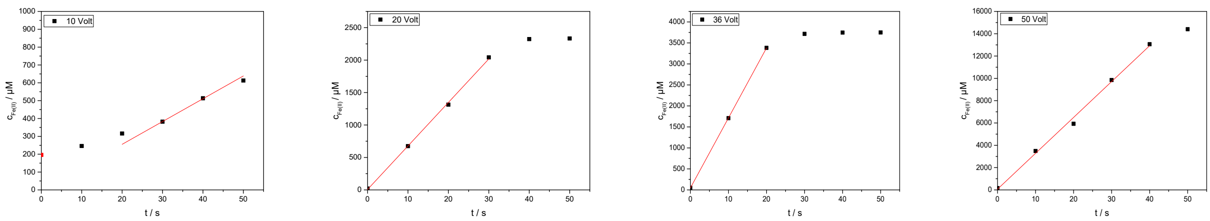

Figure S19.: Concentration-time-profiles of the iron(II) generation under illumination of the ferrioxalate solution. Reaction conditions: 50 mL ferrioxalate solution. Internal illumination with the amplifier EAP-01. 320W. 76 WLEs. Different amplifier voltages (10 V to 50 V).

Table S7.: The determined photon flux density q_p, light power density P_{light}, total light power P_{light}, power consumption P_{el} and wall plug efficiency WPE of the internal irradiation system (EAP-01. 320W) in a reaction volume of 50 mL.

Number of	Voltage U /	q_p / µM/s	P_{light} / W/L	P_{light} / W	P_{el} / W	WPE / %

WLE	V					
10	10	0.99	0.33	0.02	8.4	0.19
10	20	10.38	3.40	0.17	13.6	1.25
10	30	27.17	8.90	0.45	20.7	2.15
10	40	29.14	9.55	0.48	30.8	1.55
10	50	49.06	16.08	0.80	43	1.87
20	10	5.73	1.88	0.09	9.6	0.98
20	20	23.65	7.75	0.39	15.5	2.50
20	36	62.28	20.41	1.02	28.8	3.54
20	50	156.83	51.40	2.57	45.7	5.62
40	10	8.00	2.62	0.13	10.7	1.22
40	20	46.75	15.32	0.77	17.3	4.43
40	36	101.44	33.25	1.66	32.2	5.16
40	50	238.40	78.13	3.91	51.2	7.63
60	50	286.44	93.88	4.69	58.9	7.97
76	10	8.45	2.77	0.14	11.5	1.20
76	20	55.40	18.16	0.91	19.8	4.58
76	36	137.69	45.13	2.26	36	6.27
76	50	265.78	87.11	4.36	57	7.64

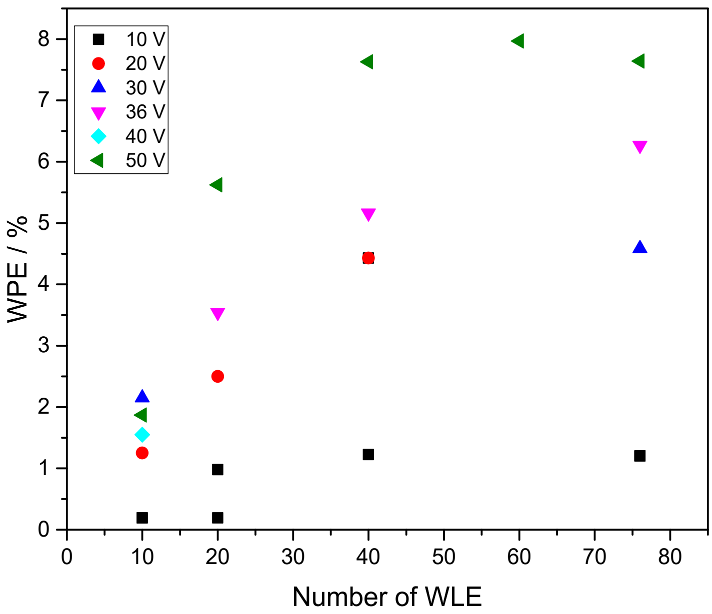

Figure S20.: Wall plug efficiency of the internal irradiation system (EAP-01) in dependence of the number of WLE at different amplifier voltages U.

1.4. Internal illumination: Amplifier: EAP-T0

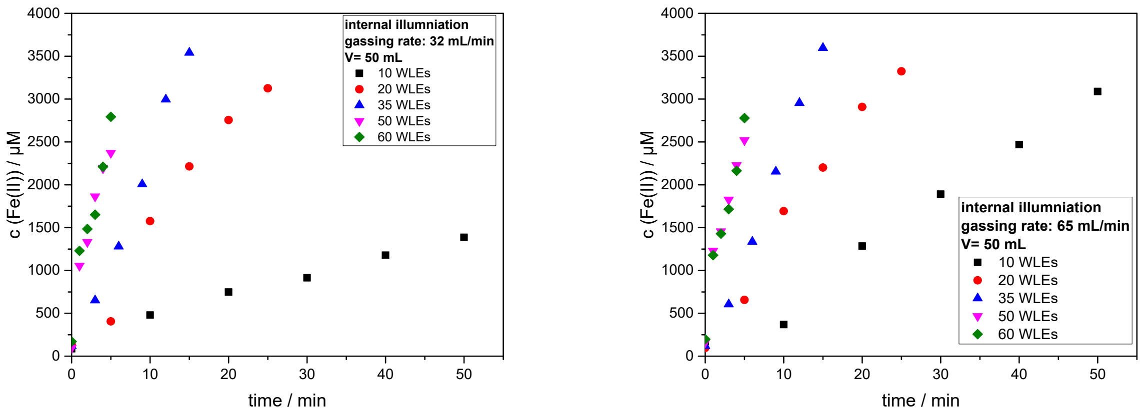

Figure S21.: Concentration-time-profiles of the iron(II) generation under illumination of the ferrioxalate solution. Reaction conditions: 50 mL ferrioxalate solution. Internal illumination with the amplifier EAP-T0. 10 WLE to 76 WLEs. Oxygen gassing rate: 32 mL min^{-1} and 65 mL min^{-1}.

Table S8.: The determined photon flux density q_p, light power density P_{light}, total light power P_{light}, power consumption P_{el} and wall plug efficiency WPE of the internal irradiation system (EAP-T0) in a reaction volume of 50 mL.

Number of WLE	q_p / µM/s	P_{light} / W/L	P_{light} / W	P_{el} / W	WPE / %	P_{WLE} / W/WLE
10	112.20	29.76	1.49	12.06	12.33	2.98
20	174.30	46.23	2.31	13.92	16.61	2.31
35	287.31	76.21	3.81	16.70	22.81	2.18
50	407.05	107.97	5.40	19.49	27.70	2.16
60	442.15	117.28	5.86	21.34	27.47	1.95

2. Reduction of nitrobenzene

2.1. External illumination: M365LP1

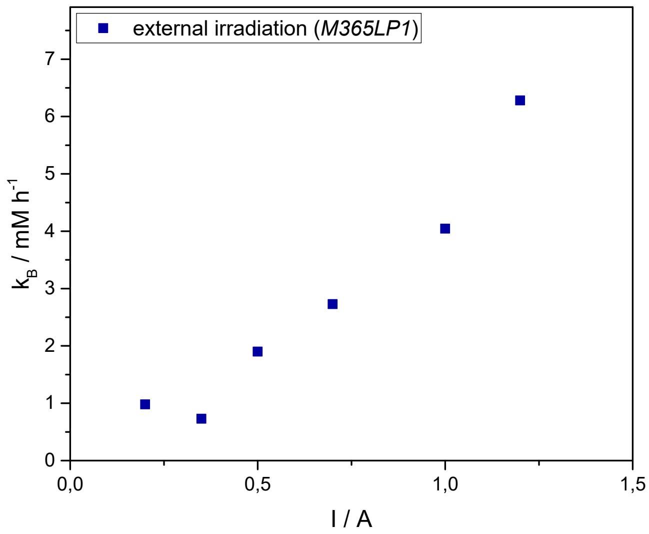

Figure S22.: Aniline formation rates (k_B) during the photocatalytic reduction of nitrobenzene in dependence of LED driver current of the external illumination systems (M365LP1).

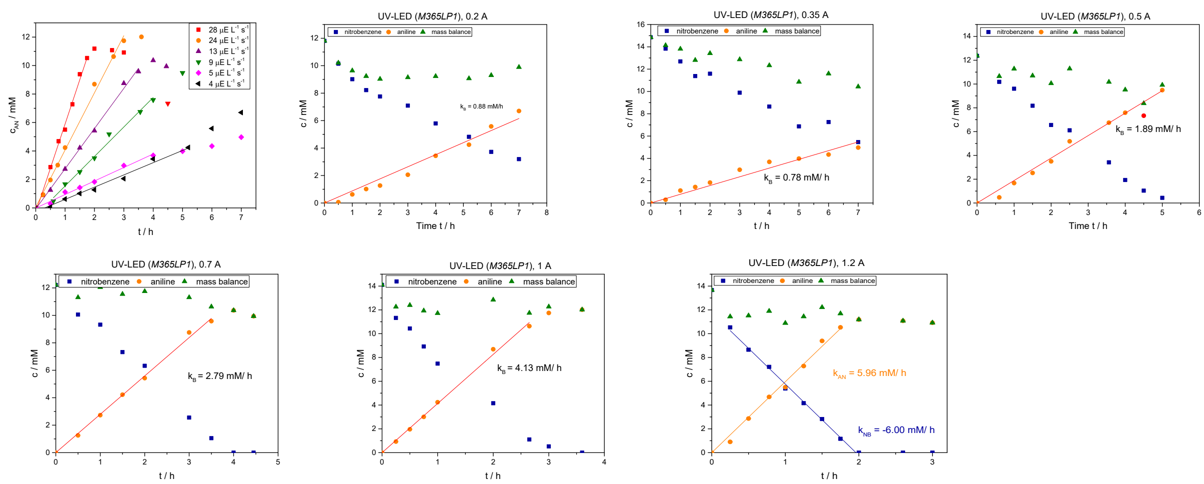

Figure S23.: Concentration-time-profiles during the photocatalytic reduction of nitrobenzene in 2-propanol with UV-LED (M365LP1) at different light intensity (LED driver current). Reaction condition: 365 nm. 2 g L^{-1} TiO_2. room temperature.

2.2. External illumination: SOLIS-365C

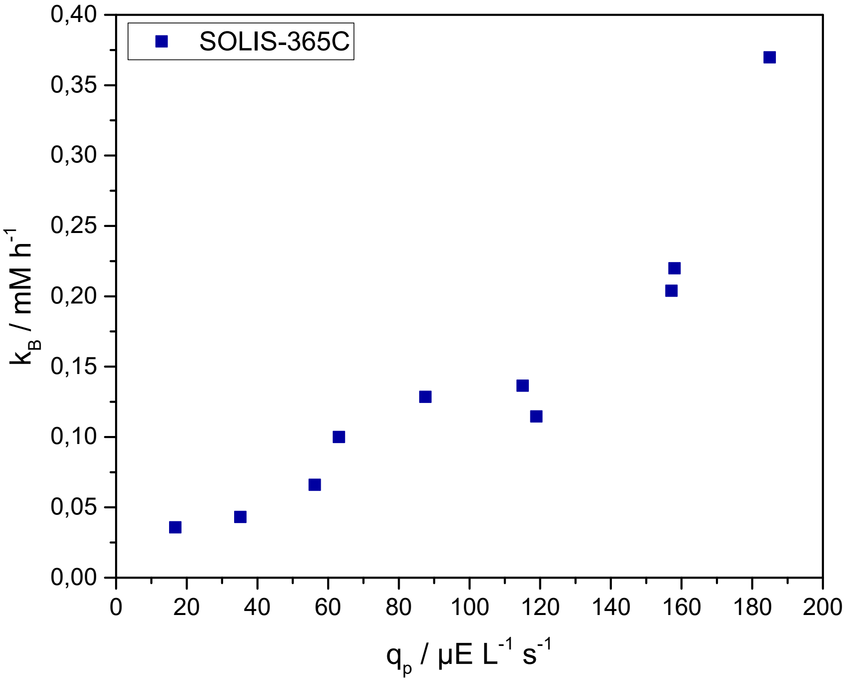

Figure S24.: Aniline formation rates (k_B) during the photocatalytic reduction of nitrobenzene in dependence of photon flux density q_p of the external illumination systems (SOLIS-365C).

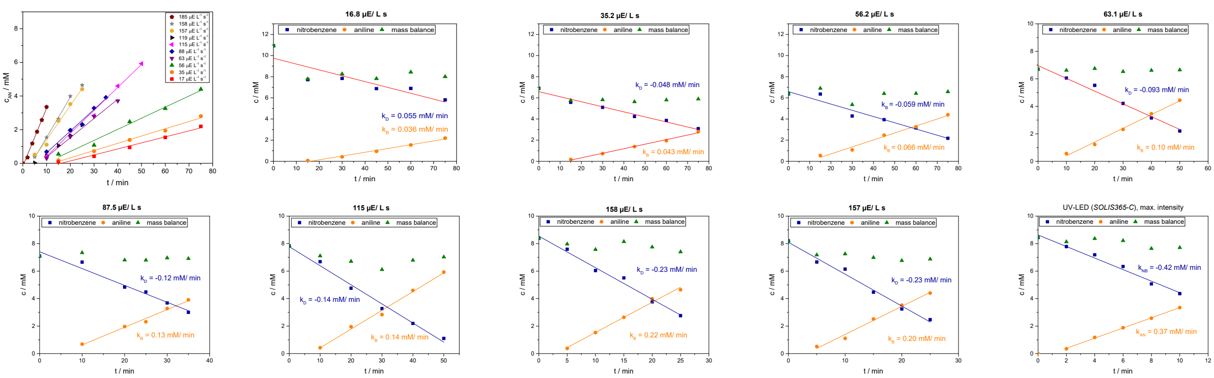

Figure S25.: Concentration-time-profiles during the photocatalytic reduction of nitrobenzene in 2-propanol with UV-LED (SOLIS-365C) at different light intensity. Reaction condition: 365 nm. 2 g L^{-1} TiO_2. room temperature.

2.3. Internal illumination: EAP-00

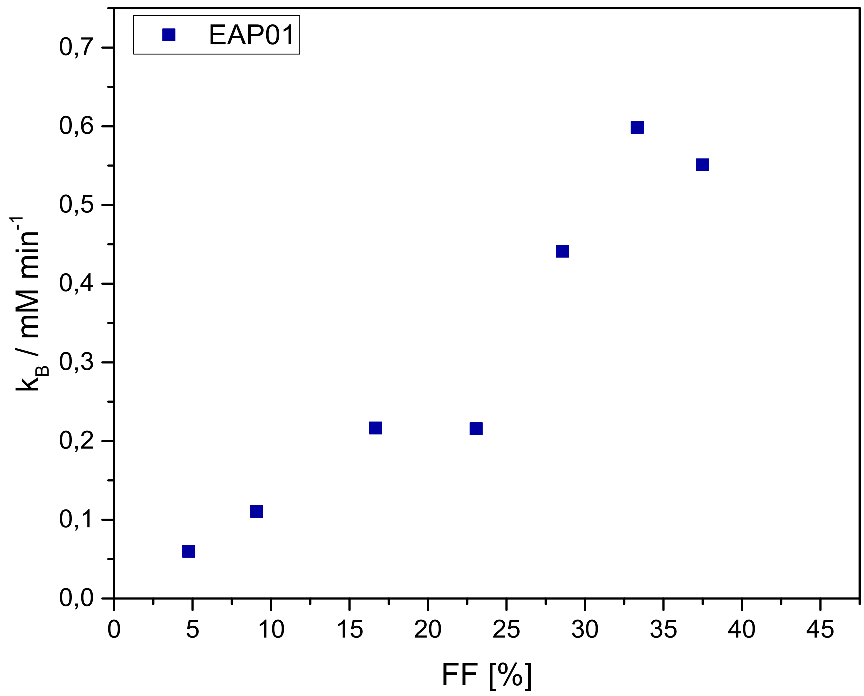

Figure S26.: Aniline formation rates of the photocatalytic reduction of nitrobenzene in dependence of FF of the internal illumination systems (EAP-00. 100 W).

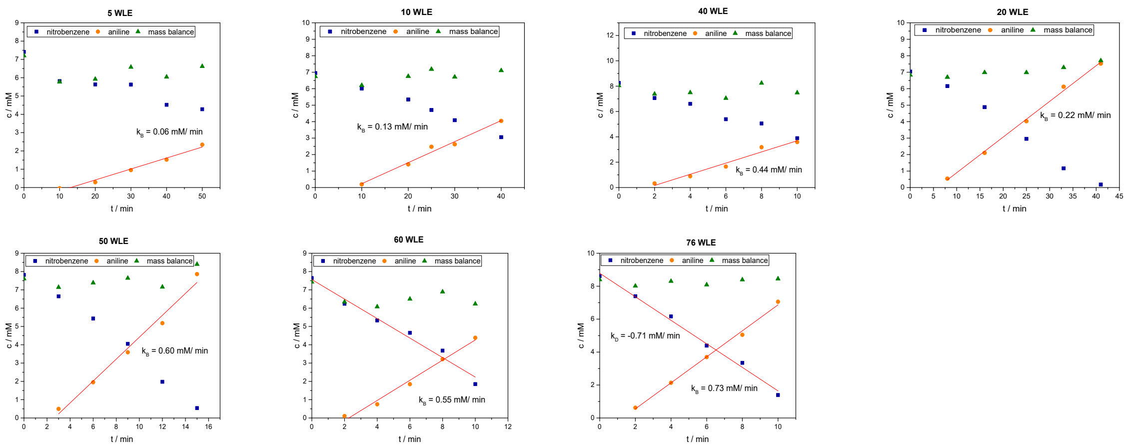

Figure S27.: Concentration-time-profiles during the photocatalytic reduction of nitrobenzene in 2-propanol with the amplifier EAP-00. 100 W. Different numbers of WLE were used (5 to 76 WLEs). Reaction condition: 365 nm. 2 g L^{-1} TiO_2. room temperature.

Experiments with different liquid volumes

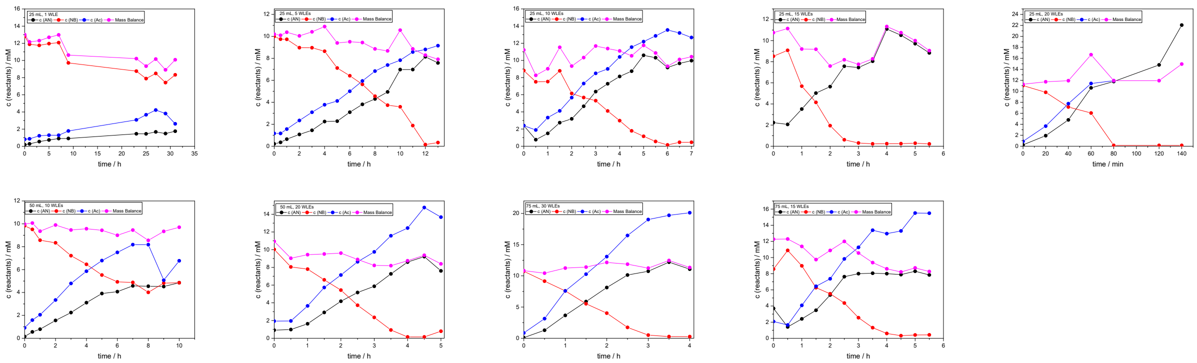

Figure S28.: Concentration-time-profiles during the photocatalytic reduction of nitrobenzene in 2-propanol. Amplifier: EAP-00. 50 W. Different solution volume were investigated (25 mL, 50 mL and 75 mL). Different numbers of WLE (1 WLE to 30 WLE) were used for each liquid volume. Reaction condition: 365 nm. 2 g L^{-1} TiO_2. room temperature.

2.4. Internal illumination: EAP-01

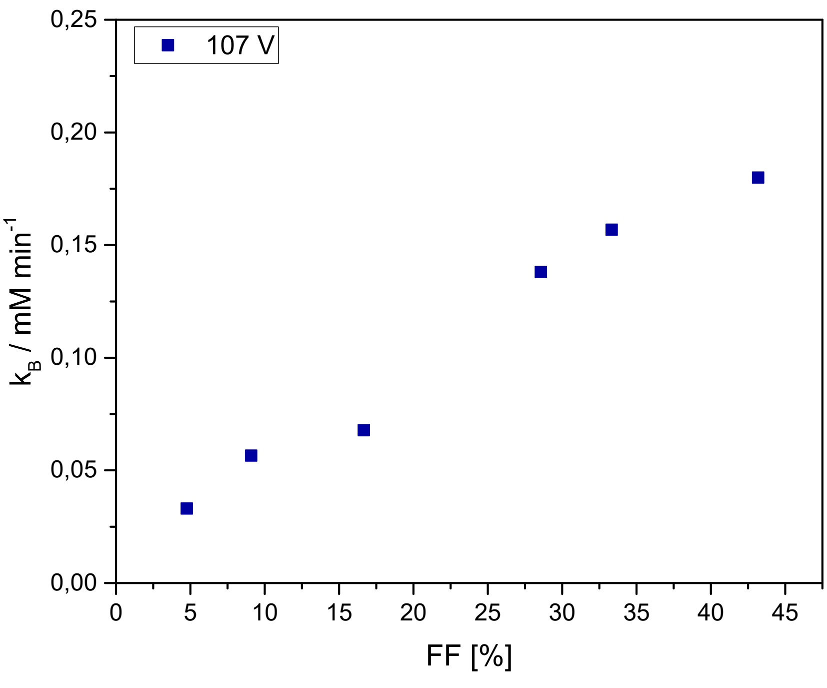

Figure S29.: Aniline formation rates (k_B) during the photocatalytic reduction of nitrobenzene in dependence of the fill factor (FF) of the internal illumination systems (EAP-01. 320 W).

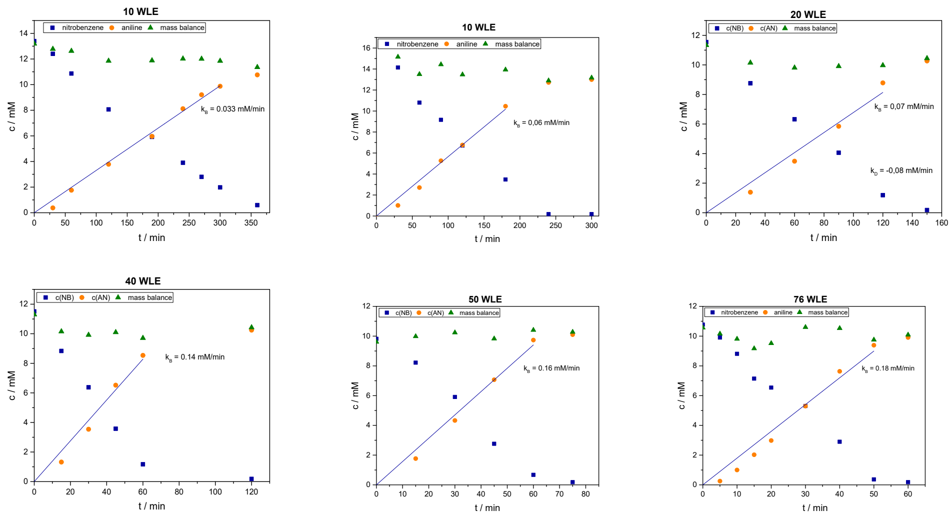

Figure S30.: Concentration-time-profiles during the photocatalytic reduction of nitrobenzene in 2-propanol. Amplifier: EAP-01. 320 W. Different numbers of WLE were used (5 to 76 WLEs). Reaction condition: 365 nm. 2 g L^{-1} TiO_2. room temperature.

3. Comparison between external and internal illumination

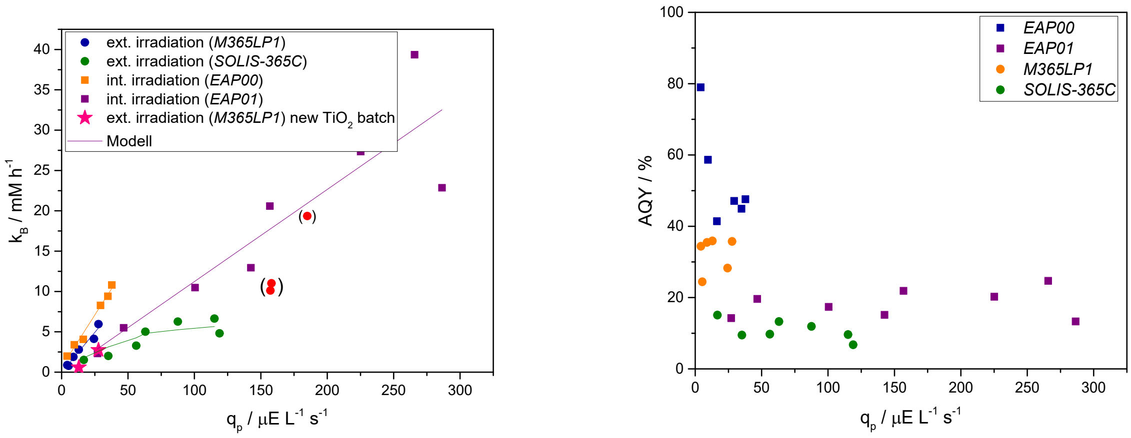

Figure S31.: Right: Comparison between every irradiation system (MP365LP1. SOLIS-365C. EAP-00 (100 W) and EAP-01 (320 W)) of the photocatalytic reduction of nitrobenzene. Left: Formation rates of aniline (k_B) in dependence of the photon flux density q_p. Right: Determined apparent quantum yield AQY in dependence of photon flux density q_p.

4. Investigation of different TiO_2 concentrations

4.1. External Illumination: SOLIS-365C

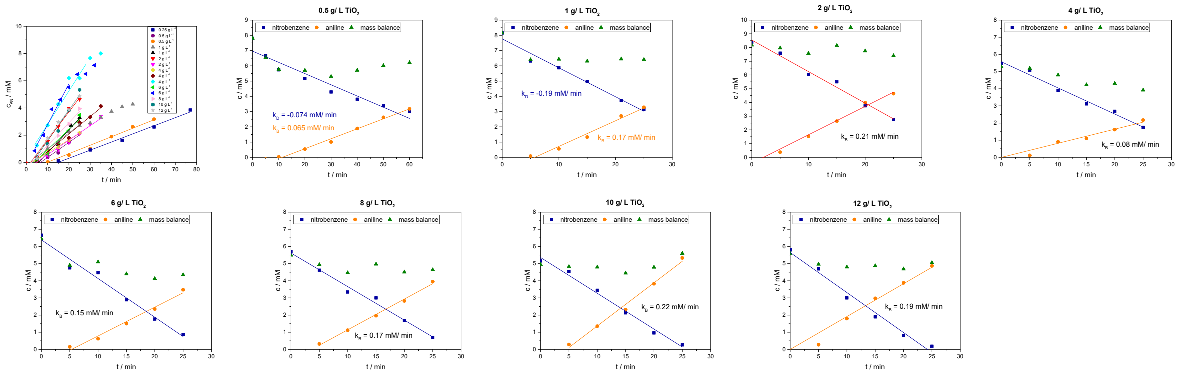

Figure S32.: Concentration-time-profiles during the photocatalytic reduction of nitrobenzene in 2-propanol with UV-LED (SOLIS-365C) at the maximum light intensity. Different TiO_2 concentrations were investigated (0.5 g L^{-1} to 12 g L^{-1}). Reaction condition: 365 nm irradiation wavelength. room temperature.

4.2. Internal Illumination: EAP01

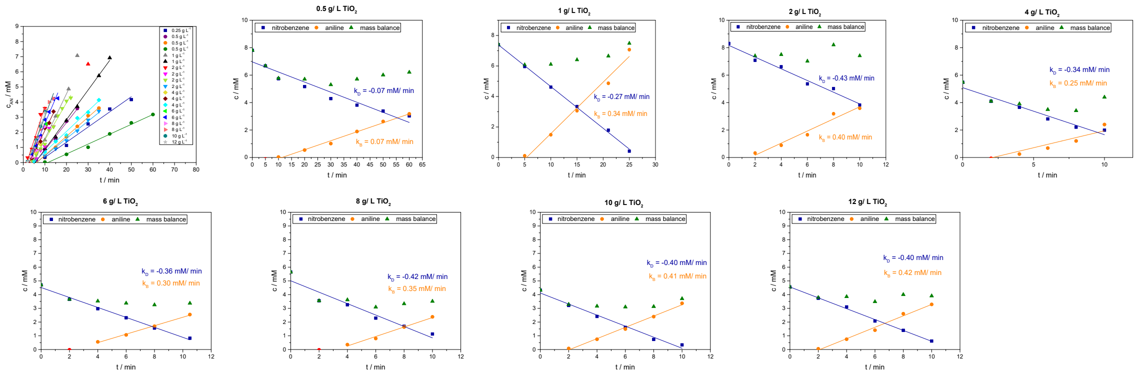

Figure S33.: Concentration-time-profiles during the photocatalytic reduction of nitrobenzene in 2-propanol. Amplifier EAP-01. 320 W. Different TiO_2 concentrations were investigated (0.5 g L^{-1} to 12 g L^{-1}). Reaction condition: 365 nm irradiation wavelength. room temperature.

5. Investigation of different NB concentrations

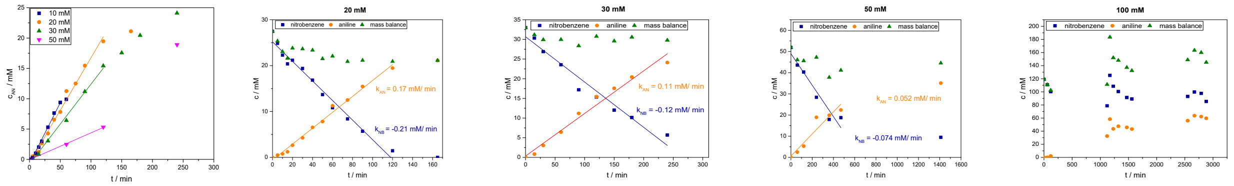

Figure S34.: Concentration-time-profiles during the photocatalytic reduction of nitrobenzene in 2-propanol. Amplifier: EAP-00. 100 W. Different NB concentrations were investigated (10 mM to 100 mM). Reaction condition: 365 nm irradiation wavelength. 2 g L^{-1} TiO_2. room temperature.

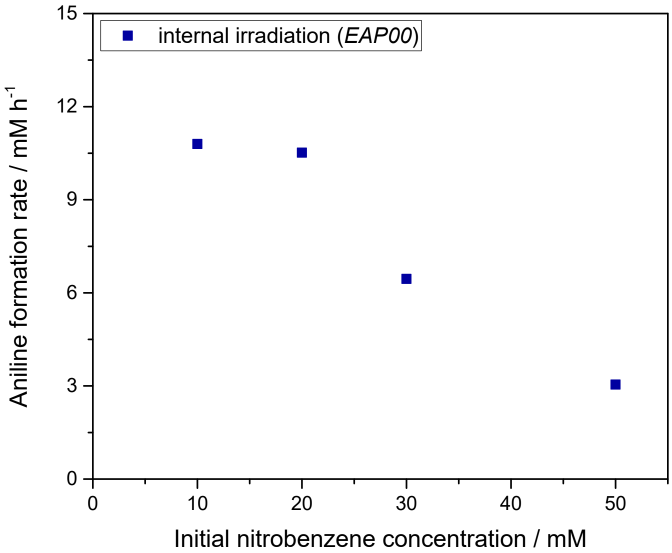

Figure S35.: Aniline formation rates (k_B) during the photocatalytic reduction of nitrobenzene in dependence of different NB concentrations (10 mM to 50 mM). Reaction condition: 76 WLEs. 365 nm. 2 g L^{-1} TiO_2. room temperature. Amplifier EAP-00.

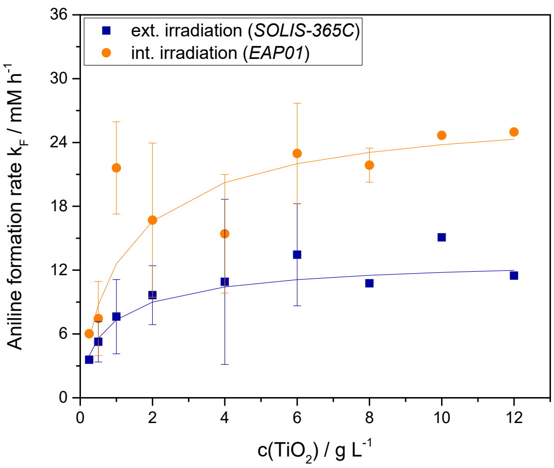

Figure S36.: Comparison between internal (EAP-01) and external (SOLIS-365C) illumination of the aniline formation rates for the photocatalytic reduction of nitrobenzene in dependence of different TiO_2 concentrations (0.5 g L^{-1} to 12 g L^{-1}).

6. Quantum yield of the experiment for the reduction of NB using amplifier EAP-00

Table S9.: Calculation of apparent quantum yield (AQY) for the reduction of nitrobenzene with the amplifier EAP-00 at different volumes (25 mL, 50 mL, 75 mL).

Volume [mL]	Number of WLE	FF / %	q_p / µM/s	k_{AN} / mM/min	AQY / %
25	1	2.2	0.22	0.0017	77.7
25	5	10.0	3.0	0.016	55.0
25	10	18.1	8.1	0.036	45.0
25	15	24.9	8.6	0.076	88.0
25	20	30.7	14.7	0.101	68.5
50	10	10.0	3.8	0.020	51.3
50	20	18.1	6.8	0.036	52.2
75	15	10.0	3.3	0.017	50.0
75	30	18.1	6.7	0.048	71.8

7. Pictures of reaction systems

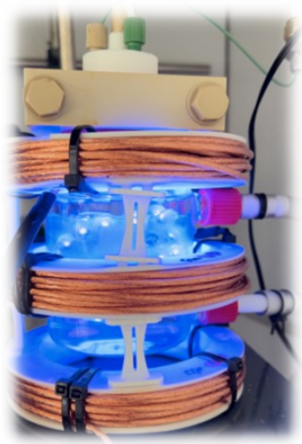

Figure S37.: Newly developed 100 mL borosilicate double-jacketed reaction vessel (Schott flask) for precise temperature control, used in the experiments with the EAP-01 and EAP-T0 amplifiers.