Supporting Information

Every Photon Counts: Understanding and Optimizing Photon Paths in Luminescent Solar Concentrator-based Photomicroreactors (LSC-PMs)

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LSC-PM Manufacturing

The LSC-PM devices were produced as previously reported.[1]

Two slabs of Lumogen F Red 305 (LR305)-doped PDMS (Dow Corning Sylgard 184, ratio 10:1 base:curing agent) were bonded together after an oxygen plasma treatment (1 min, 30W): a 2 mm thick layer with the reaction channel profile and a flat slab of 1 mm thickness as cover. The channel layer is obtained by casting PDMS in a 3D-printed mold (printed with a Felixprinters Felix Pro 2) with the positive relief of the channel design, while the cover layer was the result of the PDMS casting in a Petri dish. A schematic overview of the complete process is presented in Figure S1. The resulting channel have a rectangular cross-section and are 0.5 mm width and 1mm tall (see Figure S2).

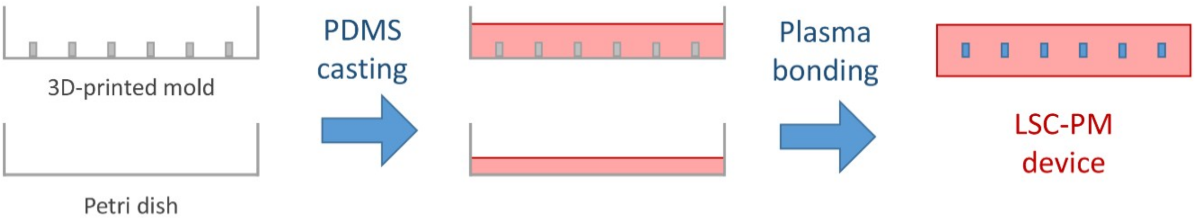

Figure S1. LSC-PM device process overview. First, LR305-doped PDMS is cast in a Petri dish modified with the 3D-printed mold. Then, the polymer is thermally cured and the two pieces are bonded with plasma oxygen, resulting in the final device.

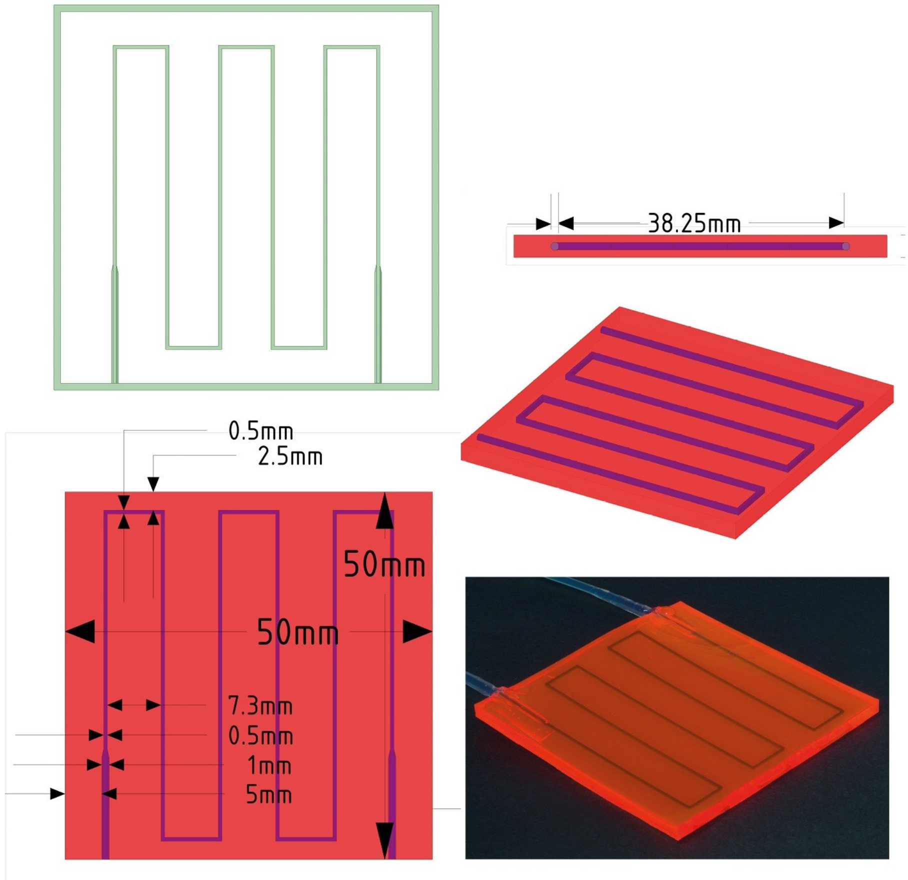

Figure S2 Designs and photograph of the LSC-PM.

Model validation

Source code

The source-code of the python scripts used for the simulation is freely available on Git-hub (https://github.com/dcambie/pvtrace).

Simulations were run with "/pvtrace/scripts/LSC-PM/run_simulation.py", while to calculate the APPTDs, the "/pvtrace/scripts/LSC-PM/abalyse_simulation.py" script was used. For all the simulations in the model validation section the "5x5_6ch_squared" model reactor was used, that was designed to match the experimental design. The channel geometry of all the simulated reactor can be found in the relevant file in "/pvtrace/data/reactors/".

The model assumes a quantum yield for Red 305 in PDMS of 0.95 and an AM 1.5G solar spectrum irradiating with normal incidence the top surface of the LSC-PM. The luminophore particles are assumed to be homogenously dispersed throughout the LSC-PM; thus, the absorption spectrum is constant throughout the device. The refractive index of the lightguide is based on that of PDMS and is assumed constant in the range of wavelengths considered (350-700 nm). The quantum yield of the dye is assumed constant regardless the incident photon intensity and the luminescent emission is isotropic. For the reaction channels, methylene blue (the photocatalyst) is assumed to be the only absorbing species is solution. Scattering effects are not considered in simulations.

All simulations were performed with 100k photons as this quantity offers a good tradeoff between accuracy and computation time. While the duration of the simulation depends on factors like the dye doping, the number of elements included in the scene and the average number of steps for photon, a typical simulation of a 5x5cm device with a 200ppm LR305 doping took about 1 hour (with in-memory database). It is well known that, due to the stochastic nature of Monte Carlo simulations, the standard deviation of the results decreases with the square root of the number of repetitions. This trend was observed also in our case, as highlight by the exponential trend (close to $x^{-0.5}$) in Figure S3, where the same simulation was repeated 5 times with different number of photons to estimate the error associated with each photon fate at different photon-counts. Intuitively, the photon fate with less evaluation steps and with higher photon fraction (e.g. Solar photons transmitted at the bottom) are characterized by lower errors.

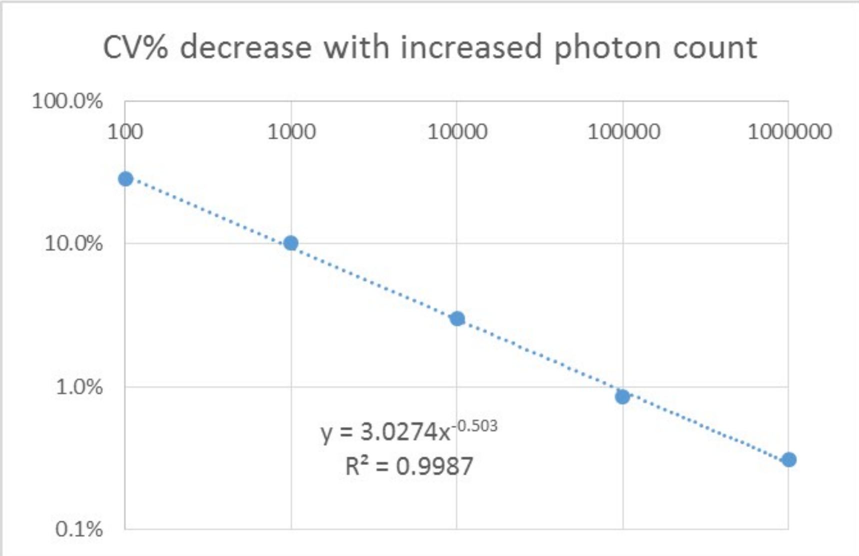

Figure S3 Decreasing error with the increased photon number per simulation.

Photon count	Total photons	Losses	Luminescent		Solar		Channels			Average
			Edges	Apertures	Top	Bottom	Direct	Luminescent		
100	0.0%	39.9%	63.2%	20.9%	44.5%	1.9%	44.5%	15.3%		28.8%
1k	0.1%	17.1%	15.8%	11.8%	8.2%	3.3%	18.4%	6.5%		10.2%
10k	0.0%	4.4%	4.8%	3.0%	2.6%	0.9%	3.9%	4.1%		3.0%
100k	0.0%	0.9%	1.9%	0.8%	0.9%	0.3%	1.7%	0.3%		0.8%
1M	0.0%	0.2%	0.3%	0.2%	0.7%	0.1%	0.9%	0.1%		0.3%

Reflections

Experimental

For the measurement of the reflectance, a Perkin Elmer Lambda 750 UV-VIS-NIR spectrophotometer with a Universal Reflectance Accessory was used. In particular, the device was irradiated with an angle of incidence of 15° and the reflection was measured at 30°. The angular distribution of the reflected beam and its spectral distribution (evidencing the luminophore absorption) are reported in Figure S4.

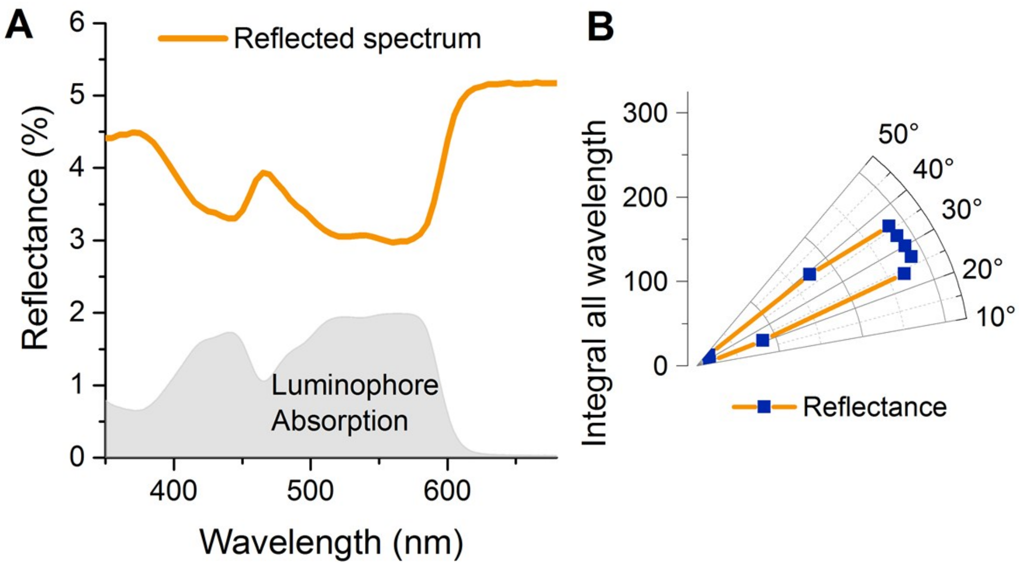

*Figure S4 **A** Spectral distribution of a high-doping LSC-PM showing the impact of the luminophore absorption in the bottom reflected photons. **B** Angular distribution of the light reflected by the LSC-PM.*

Simulation

In normal conditions, the model printout does not allow to split the contribution from first and second surfaces reflections. To measure the number of photons reflected by the top surface, the following query was executed on the photon database at the end of the simulation:

```
SELECT MAX(uid) FROM photon GROUP BY pid HAVING uid IN (SELECT uid FROM state
WHERE ray_direction_bound = "Out" AND surface_id='top' AND intersection_counter = 1
GROUP BY uid);
```

The expected reflectance for normal irradiation of PDMS (n=1.41) according to Fresnel equations would be:

$$R = \left(\frac{n-1}{n+1}\right)^2$$

$$R = \left(\frac{n_{\mathrm{PDMS}} - n_{air}}{n_{\mathrm{PDMS}} + n_{air}}\right)^2 = \left(\frac{1.41-1}{1.41+1}\right)^2 = 2.91$$

The raw results of the simulation are the following:

LR305 doping (ppm)	Total photons	Losses	Luminescent		Solar		Channels		Top		Reflections		
			Edges	Apertures	Top	Bottom	Direct	Luminescent	Reflections		Total	Top	Bottom
0	100000	308	0	0	5628	90303	3761	0	2956		5.6%	3.0%	2.7%
10	99997	846	1860	1988	5278	83945	3650	2430	2992		5.3%	3.0%	2.3%
20	99993	1310	3157	3899	4843	78689	3503	4593	2852		4.8%	2.9%	2.0%
30	100000	1657	4351	5667	4786	73854	3361	6324	3005		4.8%	3.0%	1.8%
40	99993	2011	5396	7045	4696	69491	3387	7968	2964		4.7%	3.0%	1.7%
50	99989	2385	6011	8370	4547	66221	3390	9065	2899		4.5%	2.9%	1.6%
60	99989	2697	6645	9335	4358	63431	3303	10221	2939		4.4%	2.9%	1.4%
70	99991	2930	7336	10287	4276	60808	3202	11153	2863		4.3%	2.9%	1.4%
80	99987	3193	7734	11404	4232	58221	3193	12011	2897		4.2%	2.9%	1.3%
90	99989	3424	8228	11829	4359	56272	3153	12725	2994		4.4%	3.0%	1.4%

LR305 doping (ppm)	Total photons	Losses	Luminescent		Solar		Channels		Top		Reflections		
			Edges	Apertures	Top	Bottom	Direct	Luminescent	Reflections		Total	Top	Bottom
100	99989	3555	8554	12817	4038	54503	3008	13514	2870		4.0%	2.9%	1.2%
110	99986	3736	9181	13197	4067	52870	3085	13851	2897		4.1%	2.9%	1.2%
120	99991	3880	9382	13875	4010	51489	2967	14388	2845		4.0%	2.8%	1.2%
130	99988	4214	9831	14481	4069	49532	2972	14889	2903		4.1%	2.9%	1.2%
140	99988	4227	9781	15053	3933	48640	2964	15390	2850		3.9%	2.9%	1.1%
150	99986	4415	10232	15253	4086	47330	2963	15708	2961		4.1%	3.0%	1.1%
160	99983	4313	10440	15659	4073	46609	2859	16032	3014		4.1%	3.0%	1.1%
170	99990	4583	10554	16174	3997	45463	2880	16340	2859		4.0%	2.9%	1.1%
180	99989	4671	10583	16391	4019	44715	2847	16763	2947		4.0%	2.9%	1.1%
190	99988	4765	10818	16728	3894	44076	2802	16906	2841		3.9%	2.8%	1.1%
200	99989	4768	11068	17214	3871	43276	2741	17051	2865		3.9%	2.9%	1.0%
210	99985	5060	11127	17293	3937	42677	2750	17141	2932		3.9%	2.9%	1.0%
220	99978	5129	11129	17517	3920	41948	2647	17691	2891		3.9%	2.9%	1.0%
230	99984	5047	11434	17795	3880	41424	2592	17812	2865		3.9%	2.9%	1.0%
240	99986	5233	11641	17876	3963	40581	2720	17972	2943		4.0%	2.9%	1.0%
250	99988	5230	11527	18210	3917	40241	2659	18204	2944		3.9%	2.9%	1.0%

Transmission

Experimental

The transmission spectra were measured by irradiating 5x5cm LSC-PM placed on the opening of an integrating sphere (Labsphere, Inc. LMS 1050) with solar simulated light (LS0110-100, L.O.T.-Oriel GmbH & Co.) reflected from a prism. In figure Figure S5 the transmission spectra of the different devices. Both the dye absorption and the bottom emission are clearly visible.

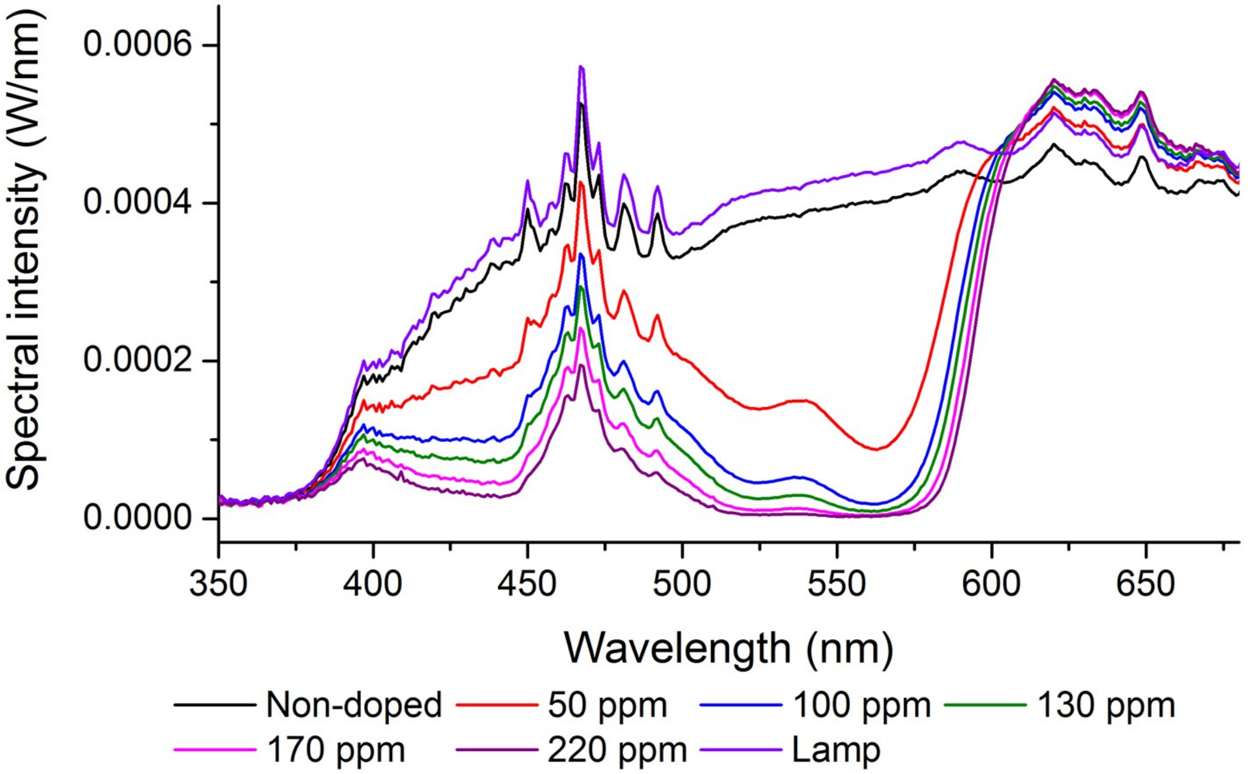

Figure S5 Transmission spectra of LSC-PMs with different dye doping. It's notable the decrease in transmission due to the dye absorption in the 400-600 nm range and the increase due to luminescent photons leaving the device from the bottom aperture at wavelengths longer than 600 nm.

Simulation

For the transmission spectra simulation, the 5x5cm reactor was modelled considering air in the channel (refractive index=0). This allows the accurate simulation of the luminescent photons emitted out of the escape cone.

The raw results of the simulation are the following:

LR305 doping (ppm)	Total photons	Losses	Luminescent			Solar			Transmission		
			Edges	Top	Bottom	Top	Bottom		Total	Luminescent	Solar
0	100000	303	0	0	0	6020	93677		93.7%	0.0%	93.7%
10	99560	1033	3007	1365	1379	5737	87039		88.8%	1.4%	87.4%
20	99324	1536	5246	2722	2727	5474	81619		84.9%	2.7%	82.2%
30	99112	2172	7233	3760	3863	5187	76897		81.5%	3.9%	77.6%
40	98855	2613	8966	4945	4729	4999	72603		78.2%	4.8%	73.4%
50	98748	2960	10427	5661	5659	4925	69116		75.7%	5.7%	70.0%
60	98551	3448	11674	6320	6499	4835	65775		73.3%	6.6%	66.7%
70	98535	3626	12753	7116	7165	4640	63235		71.4%	7.3%	64.2%
80	98421	3903	13624	7743	7574	4571	61006		69.7%	7.7%	62.0%
90	98299	4289	14538	8135	8120	4521	58696		68.0%	8.3%	59.7%
100	98205	4451	14915	8705	8583	4598	56953		66.7%	8.7%	58.0%
110	98128	4595	15614	9292	8917	4376	55334		65.5%	9.1%	56.4%
120	98087	4990	16080	9611	9287	4567	53552		64.1%	9.5%	54.6%

LR305 doping (ppm)	Total photons	Losses	Luminescent			Solar			Transmission		
			Edges	Top	Bottom	Top	Bottom		Total	Luminescent	Solar
130	98050	5071	16872	9968	9573	4387	52179		63.0%	9.8%	53.2%
140	97929	5424	17201	10322	9859	4247	50876		62.0%	10.1%	52.0%
150	97838	5586	17645	10442	10233	4257	49675		61.2%	10.5%	50.8%
160	97875	5675	18051	10959	10172	4275	48743		60.2%	10.4%	49.8%
170	97759	5746	18361	11145	10510	4267	47730		59.6%	10.8%	48.8%
180	97779	5836	18919	11234	10651	4242	46897		58.9%	10.9%	48.0%
190	97746	5935	18869	11534	10941	4143	46324		58.6%	11.2%	47.4%
200	97730	5894	19403	11799	11049	4163	45422		57.8%	11.3%	46.5%
210	97638	6149	19321	12018	11236	4170	44744		57.3%	11.5%	45.8%
220	97659	6132	19775	12305	11220	4266	43961		56.5%	11.5%	45.0%
230	97526	6401	19590	12452	11557	4066	43460		56.4%	11.9%	44.6%
240	97495	6591	19856	12525	11556	4065	42902		55.9%	11.9%	44.0%
250	97594	6569	20257	12565	11722	4113	42368		55.4%	12.0%	43.4%

Edge emissions

Experimental

For the edge emission measurement, a 300 W solar simulator (LS0110-100, L.O.T.-Oriel GmbH & Co.) equipped with filters to approximate the 1.5 air mass solar spectrum (AM 1.5), and a 10 in integrating sphere (Labsphere, Inc. LMS 1050) coupled with a diode array detector (RPS900, International Light) with a sample holder matching the device sizes (5×5×0.3 cm^3) were utilized.

Simulation

For the simulations with methylene blue (MB) in the channels (Figure 4B in the manuscript), increasing concentration of MB in acetonitrile were simulated in 50, 100 and 200 ppm LSC-PM.

The raw results of the simulation **for the 50 ppm dye-doped** devices are the following:

MB loading (M)	Total photons	Losses	Luminescent		Solar		Channels			Edge emissions
			Edges	Apertures	Top	Bottom	Direct	Luminescent		
1.00E-05	99514	2885	11301	10119	4544	68755	343	1572		11.4%
1.26E-05	99602	2828	11057	9967	4597	68784	441	1937		11.1%
1.58E-05	99693	2840	10717	9771	4654	68952	507	2259		10.8%
2.00E-05	99693	2772	10539	9665	4558	68802	643	2720		10.6%
2.51E-05	99748	2718	10295	9645	4420	68738	793	3146		10.3%
3.16E-05	99809	2669	9872	9569	4379	68818	940	3573		9.9%
3.98E-05	99871	2674	9296	9453	4554	68425	1136	4337		9.3%
5.01E-05	99901	2565	9139	9407	4502	68196	1296	4798		9.1%
6.31E-05	99934	2561	8656	9243	4449	67972	1588	5467		8.7%
7.94E-05	99953	2447	8277	8885	4618	67920	1767	6040		8.3%
1.00E-04	199908	5089	15768	17809	9126	134953	4083	13083		7.9%
1.26E-04	99975	2521	7351	8685	4495	67512	2286	7127		7.4%

MB loading (M)	Total photons	Losses	Luminescent		Solar		Channels			Edge emissions
			Edges	Apertures	Top	Bottom	Direct	Luminescent		
1.58E-04	99983	2463	6891	8787	4520	67052	2545	7725		6.9%
2.00E-04	99986	2441	6784	8626	4409	67094	2675	7957		6.8%
2.51E-04	99993	2372	6303	8524	4422	67254	2854	8264		6.3%
3.16E-04	99994	2428	6247	8344	4527	66495	3184	8769		6.2%
3.98E-04	99995	2407	6036	8175	4433	66444	3348	9152		6.0%
5.01E-04	99998	2365	5926	8160	4392	66351	3553	9251		5.9%
6.31E-04	99987	2299	5889	8073	4374	66380	3657	9315		5.9%
7.94E-04	99993	2385	5658	8079	4450	65975	3913	9534		5.7%
1.00E-03	99992	2410	5633	8067	4531	65479	4174	9700		5.6%

The raw results of the simulation **for the 100 ppm dye-doped** devices are the following:

MB loading (M)	Total photons	Losses	Luminescent		Solar		Channels			Edge emissions
			Edges	Apertures	Top	Bottom	Direct	Luminescent		
1.00E-05	99405	4334	16112	15338	4237	56647	342	2400		16.2%
1.26E-05	99453	4268	15788	15331	4100	56720	424	2829		15.9%
1.58E-05	99519	4186	15373	15163	4226	56634	537	3409		15.4%
2.00E-05	99637	4178	15122	15065	4238	56475	590	3971		15.2%
2.51E-05	99681	4166	14379	14930	4210	56456	782	4761		14.4%
3.16E-05	99754	4046	13889	14727	4241	56395	875	5585		13.9%
3.98E-05	99791	3970	13515	14498	4251	56154	1024	6386		13.5%
5.01E-05	99861	4017	13028	14379	4224	55690	1280	7247		13.0%
6.31E-05	99911	3809	12346	14108	4164	55813	1494	8178		12.4%
7.94E-05	99911	3877	11524	14021	4107	55635	1766	8985		11.5%
1.00E-04	99941	3881	11206	13624	4143	55385	1897	9810		11.2%
1.26E-04	99967	3890	10599	13772	4128	54843	2128	10608		10.6%
1.58E-04	99972	3851	10073	13135	4161	55060	2313	11379		10.1%
2.00E-04	99983	3735	9510	13238	4145	54867	2558	11932		9.5%
2.51E-04	99980	3612	9227	13043	4132	54891	2726	12349		9.2%
3.16E-04	99989	3685	8933	12741	4224	54498	3007	12901		8.9%
3.98E-04	99984	3512	8621	12858	4164	54385	3078	13367		8.6%
5.01E-04	99988	3505	8568	12685	4131	54264	3307	13528		8.6%
6.31E-04	99986	3564	8559	12248	4137	54124	3484	13871		8.6%
7.94E-04	99991	3649	8152	12377	4164	54322	3568	13760		8.2%
1.00E-03	99991	3628	8228	12546	4128	53685	3780	13997		8.2%

The raw results of the simulation **for the 200 ppm dye-doped** devices are the following:

MB loading (M)	Total photons	Losses	Luminescent	Solar	Channels		Edge emissions

			Edges	Apertu res	Top	Bottom	Direct	Lumine scent		
1.00E-05	99204	5806	20376	20274	3985	45294	292	3182		20.5%
1.26E-05	99278	5792	19781	20405	3954	45389	368	3595		19.9%
1.58E-05	99445	5871	19650	20021	3939	45026	473	4474		19.8%
2.00E-05	99506	5606	18861	20012	3967	45150	599	5322		19.0%
2.51E-05	99596	5723	18462	19512	3974	44855	790	6285		18.5%
3.16E-05	99697	5536	17817	19525	3976	44781	842	7229		17.9%
3.98E-05	99773	5471	17164	19322	4007	44625	1013	8178		17.2%
5.01E-05	99828	5367	16501	19125	3911	44337	1187	9406		16.5%
6.31E-05	99871	5366	15348	18960	4017	44300	1398	10490		15.4%
7.94E-05	99924	5419	14617	18496	3964	44188	1583	11663		14.6%
1.00E-04	99941	5319	14077	18208	3940	43923	1734	12743		14.1%
1.26E-04	99969	5040	13381	17876	3991	43983	1972	13727		13.4%
1.58E-04	99959	5103	12788	18012	3992	43419	2151	14495		12.8%
2.00E-04	99968	4997	12249	17684	3992	43464	2367	15216		12.3%
2.51E-04	99966	5070	11701	17316	3952	43251	2516	16162		11.7%
3.16E-04	99987	5002	11071	17299	3875	43243	2622	16875		11.1%
3.98E-04	99984	4934	11078	17204	3944	43231	2723	16874		11.1%
5.01E-04	99981	4920	10620	17021	3946	43180	2747	17548		10.6%
6.31E-04	99988	4806	10486	16938	3911	43029	3035	17784		10.5%
7.94E-04	99987	4836	10425	16737	3846	43156	3142	17845		10.4%
1.00E-03	99994	4771	10525	16453	3955	42839	3295	18156		10.5%

Model optimization

5x5 cm^2 LSC-PMs

Two 5x5 cm devices were modelled: the first one matching the experimental reactor (5x5_6ch_squared) and a second one where the thickness of the channels were set to match the total device thickness minus an infinitesimal quantity epsilon, to prevent errors in the handling of the 3D geometry by the simulation algorithm (5x5_6ch_squared_fullthickness).

1x1 m^2 LSC-PMs

For the 1 square meter scaled-up devices the following reactor designs were used: “1sqm_slab”, “1sqm_1dir_10cm”, “1sqm_1dir_5cm”, “1sqm_1dir_2.5cm”, “1sqm_2dir_10cm”, “1sqm_2dir_5cm” and “1sqm_2dir_2.5cm”.

The results of the simulations included in Figure 6 in the manuscript are reported below:

Reactor design	Total photons	Losses	Luminescent		Solar		Channels	
			Edges	Apertures	Top	Bottom	Direct	Luminescent
5x5 Standard	99989	4768	11068	17214	3871	43276	2741	17051
5x5 Full thickness	999748	40616	53490	145509	38922	436829	48452	235932
No channels	90847	13067	5686	23190	3948	44956	0	0
Grid 2.5 cm	10000	439	5	1640	405	4423	304	2784

Reactor design	Total photons	Losses	Luminescent		Solar		Channels	
			Edges	Apertures	Top	Bottom	Direct	Luminescent
Grid 5 cm	99987	5264	72	18048	4054	44437	1610	26502
Grid 10 cm	99923	6229	97	19859	3953	45074	791	23922
Lines 2.5 cm	98578	6162	1161	18407	3910	44932	1519	22494
Lines 5 cm	98534	7052	1459	19768	3855	45049	793	20565
Lines 10 cm	98055	8147	1785	21141	3956	45032	404	17614

[1] D. Cambié, F. Zhao, V. Hessel, M. G. Debije, T. Noël, Angew. Chem., Int. Ed. 2017, 56, 1050.