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A leaf-inspired luminescent solar concentrator for energy efficient continuous-flow photochemistry

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Abstract: The use of solar light to promote chemical reactions holds significant potential with regard to sustainable energy solutions. While the number of visible light-induced transformations has increased significantly, the use of abundant solar light has been extremely limited. We report a leaf-inspired photomicroreactor that constitutes a merger between luminescent solar concentrators (LSCs) and flow photochemistry to enable green and efficient reactions powered by solar irradiation. This device based on fluorescent dye-doped polydimethylsiloxane collects sunlight, focuses the energy to a narrow wavelength region, and then transports that energy to embedded microchannels where the flowing reactants are converted.

The tree leaf is a complex functional element. It is capable of harvesting solar energy and transporting this energy to reaction centers for the catalytic conversion of chemical species,[1] yet it remains flexible and lightweight. The analogous harnessing of solar light for use in chemical synthesis is a long-standing dream of the chemical community.[2] In recent years, this vision has become more realistic with the introduction of visible-light photoredox catalysis,[3] which significantly expanded the scope of light-induced transformations.[4] In solar photochemistry, the traditional approach is the “flask in the sun”,[5] where photon efficiency and scale-up potentials are intrinsically limited.[6] This is particularly evident in photoredox catalysis since catalysts typically possess high extinction coefficients and the Bouguer-Lambert-Beer law limits light penetration to the outer layer of the reaction vessel. These limitations have been overcome with the use of microflow photochemistry, which uses microchannels to enable a homogeneous light irradiation.[7] Moreover, the increased photon flux enabled by the use of microflow reactors significantly reduces reaction times as compared to traditional batch reactors, indicating the photon-limited nature of the relevant transformations.[8]

Despite the environmental advantages of visible light-induced reactions, the use of direct solar light to power such transformations is, to date, extremely rare. We rationalized that the adoption of microreactor technology is a necessity for the efficient use of solar light as it renders a high surface-to-volume ratio. Yet, for cost-effective and large-scale applications, a practical way to harvest and convey photons to the reaction media is still needed. Inspired by the chromophores surrounding reaction centers in leaf light-harvesting complexes,[9] we sought a way to couple the light-gathering and converting abilities of luminophores with the photon needs of photomicroreactor channels (see Fig. 1a). From this viewpoint, the Luminescent Solar Concentrator (LSC) concept appears particularly appealing. LSCs are devices in which luminophores (e.g., fluorescent dyes or quantum dots) are dispersed in a glass or polymeric lightguide to capture solar light and direct the luminescent photons to the edges of the device.[10] At those edges, LSCs are typically coupled to photovoltaics to produce electricity.[11] Originally introduced over 30 years ago, LSCs are now used in switchable windows[12] and other applications, and could be ideal for deployment in the built environment, as they are aesthetically appealing and perform well under both direct and diffuse light.[13]

Through a synergistic merger of LSC and microflow chemistry, we aimed to develop a device where chemicals can react with sunlight in an efficient and inexpensive way, similar to the tree leaf. A requirement was that the device could make active use of diffuse light, thus being capable to operate under cloudy sky conditions, decoupling the productivity from the need for direct light. We proposed that a flow reactor could be embedded in an LSC lightguide whose luminophore was selected so that its emission profile matched the absorption spectrum of the photocatalyst or photosensitizer used for the reaction system. Due to this spectral overlap, the reaction mixture flowing in the channels experiences a photon-flux that is wavelength-concentrated and more intense than the solar light reaching the device surface. It was expected that the narrow wavelength distribution of the luminescent photons could improve the reaction selectivity, while the increased intensity of the photon flux could accelerate the apparent reaction kinetics, particularly for light-limited reactions. In addition, due to the close proximity of the reaction channels, light-guided photons travel shorter paths in our device than in traditional LSCs, resulting in reduced internal reabsorption losses.[14] Consequently, light guiding in LSC-PhotoMicroreactors (LSC-PMs) is inherently more efficient than in traditional LSCs and allows for the use of higher luminophore doping. LSC-mediated spectral down-conversion has already been applied in photovoltaics[15] and to enhance microalgae growth in photobioreactors.[16] However, by including the absorbing reaction media in the lightguide, we achieved both light concentration[17] and spectral conversion. Compared with traditional solar concentrated chemical photoreactors, the LSC-PM employs a non-optical-concentrating design that, as a result, operates at lower temperatures,[18] utilizes diffuse light, and does not require complex sun tracking.[19] These features allow for expansion of the application of solar photochemistry to higher latitudes.

To maximize the solar energy harvesting, the choice of the photocatalyst is of paramount importance. The lower the energy required to excite the catalyst, the larger the fraction of the solar spectrum that can be down-converted to match the absorption maximum. In this respect, the use of methylene blue (MB) as a photocatalyst[19a,19b] is advantageous since its low-energy absorption peak ($\lambda_{\text{max}} = 654$ nm), coupled with the down-conversion capabilities of the LSC-PM, results in a very effective use of the UV-VIS spectrum (Fig. 1b). In particular, we envisioned a combination between MB as photocatalyst and the fluorescent dye Lumogen F Red 305 (LR305) as the LSC luminophore.[21] LR305 is a perylene bisimide-based dye widely used in LSCs due to its broad absorption spectrum, excellent photoluminescent quantum yield, and...
high photostability.\textsuperscript{[114]} The coupling of LR305 with MB is particularly beneficial owing to the excellent spectral overlap between the LR305 emission and MB absorption spectra (Fig. 1c). Finally, to qualitatively demonstrate the enhanced photon-flux reaching the reaction channels, the \([4+2]\) cycloaddition of singlet oxygen to 9,10-diphenylanthracene (Fig. 1d) was used as a benchmark reaction since it displays light-limited apparent kinetics\textsuperscript{[22]} and the conversion and yield can be monitored with an inline UV-VIS spectrometer.

For the production of a LR305-doped LSC-PM, we identified polydimethylsiloxane (PDMS) as an ideal LSC-PM material by virtue of its high transparency, good thermal and chemical stabilities, and moderate refractive index (1.41). The use of PDMS in LSCs, albeit not widespread, is not unprecedented.\textsuperscript{[23]} This material is especially suited for LSC-PM since it can be easily shaped with both soft-lithography\textsuperscript{[24]} and print-and-peel techniques\textsuperscript{[25]} to produce microfluidic devices.\textsuperscript{[26]} PDMS can be readily doped with organic dyes\textsuperscript{[27]} and its chemical stability can be further increased via surface modification strategies.\textsuperscript{[27]}

For the successful coupling of the luminescent-concentrated photon flux through the device with the reaction channels, the optimization of several design parameters was crucial. We conducted an \textit{in silico} screening on the impact of several reactor design factors via a Monte Carlo ray-tracing simulation (see Supplementary Information).\textsuperscript{[28]} The aspect ratio of the channels, their relative height compared to the device thickness, and the number of channels per unit area were identified as the most important design parameters. Guided by these preliminary considerations, we designed a serpentine 150 \(\mu\)L flow microreactor made of 6 channels (500 \(\mu\)m width \(\times\) 1 mm height) in a 50 \(\times\) 50 \(\times\) 3 mm\(^3\) device (Fig. 3a).

A set of LSC-PM with LR305 doping between 10 and 250 ppm was produced and the amount of light reaching the edges of the device when irradiated from above was compared to a non-doped analogue. Notably, the bright red edges of the devices, observable by the naked eye, indicated the LSC light guiding-behaviour of the device (Supplementary Fig. 2). The device edge emission was measured in solar simulated light conditions with an integrating sphere (Fig. 2a) and the results are shown in Fig. 2b. A high edge emission was observed when the channels were filled with non-absorbing species, e.g. air or acetonitrile, that was dependent on the amount of luminophore doping. Gratifyingly, when the channels were filled with MB-solutions at different concentrations, a decrease in the edge emission was observed. This can be attributed to an increased photon absorption of guided light by the MB in the channels, providing a strong indication of the viability of the LSC-PM concept. With these results in hand, we moved toward testing the LSC-PM with the photocatalytic reaction system.

Two interwoven but distinct phenomena are responsible for the increased photon-flux in the LSC-PM channels. The first phenomenon is a luminophore-mediated spectral down-conversion of high energy photons, which have a low probability of absorption by the reaction mixture, into lower energy photons whose wavelength matches the absorption maximum of the photocatalyst. The second phenomenon is the spatial transfer of the photons to the reaction channels via total internal reflection in the polymeric

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**Figure 1 Working principle of the LSC-PM.** (A) Comparison and analogy of solar harvesting and photon transfer in a leaf and in a LSC-PM. In the leaf photosystem, the energy of the photons harvested by the antenna pigment molecules is transferred to the reaction center where it eventually reaches the primary electron acceptor. Analogously, in the LSC-PM, the photons absorbed by the embedded fluorescent dye molecules are re-emitted and then light-guided until they reach the reaction channels. (B) The Lumogen F Red 305 (LR305) mediated energy conversion of high-energy photons \textit{de facto} extends the methylene blue absorption window up to the ultraviolet region, enabling a more efficient use of the solar radiation (grey). (C) Wavelength conversion scheme of the LR305/MB based LSC-PM. The LR305 wide absorption (red) is responsible for the good light-harvesting properties of the device with respect to the solar spectrum. The spectral overlap between the emitted photons (green) and MB absorption maximum (blue) is crucial to allow effective coupling of the luminescent photons with the reaction system. (D) The singlet oxygen mediated cycloaddition of 9,10-diphenylanthracene to the corresponding endoperoxide was used as benchmark reaction.
lightguide. Essentially, the entire polymeric slab acts as a photon collector. Consequently, the reaction channels receive (i) direct incident photons and (ii) light-guided photons from the LSC photon collector. We set out to experimentally validate these two distinct phenomena in our LSC-PM design.

Firstly, we aimed to assess the role of the spectral down-conversion in increasing the overall likelihood of photon absorption by the reaction medium. Therefore, we selected a light source with a deliberate mismatch to MB’s absorption spectrum: blue LEDs emitting at a peak of 464 nm. LSC-PMs with different LR305 loadings and a non-doped control reactor were irradiated with different intensities, and the reaction conversion was measured (Fig. 3a). The non-doped reactor showed low conversion in all cases, even when the LED strip was fully powered (21% at 0.31 W of emitted light). In contrast, with the dye doped devices, an increase in conversion was observed. With the 200 ppm LSC-PM, the highest conversion measured in the non-doped reactor was reached with 1/10th of the light input (27% at 0.025 W), clearly indicating the effectiveness of the LSC-PM induced spectral conversion.

Secondly, we verified the light transport in the device by employing a modified reactor that avoided direct irradiation of the reaction mixture. The modified LSC-PM contained 2 channels (50 μL volume) spanning half of the top surface (25 × 50 mm²) that was shielded from direct incident light with opaque black cardboard. The other uncovered half of the reactor was exposed to a collimated light source (Fig. 3b), provided by a solar simulator. The non-doped reactor afforded low conversion (9%), even with a residence time of 90 seconds. This can be attributed primarily to scattering effects in the PDMS polymer. However, the LSC-PMs were able to transport light from the irradiated half to the reaction channels with an increased efficiency for higher lumophore loadings. Comparing the conversion of the 200 ppm LR305-doped LSC-PM at 90 seconds (54%), with that of the non-doped reactor translates in a 6-fold increase in light transport (see Supplementary Information for details). This result is particularly significant as the emission of the dye molecules in the irradiated region was mostly isotropic and no reflectors were applied to the device edges. Therefore, only a fraction of the generated luminescent photons was directed toward the reaction channels.

Lastly, we tested the unmodified LSC-PM design in the same solar-simulated conditions (Fig. 3c). The LR305-doping had a significant effect on the apparent reaction kinetics, with the 200 ppm dye-doped LSC-PM resulting in a more than 4-fold increase with respect to the non-doped reactor (see Supplementary Information for details).

While the use of a solar simulator has been convenient for the development phase of the LSC-PM, real solar irradiation conditions are unique and constitute the actual litmus test for our device. We therefore designed a convenient flow set-up to compare in real time the conversion in both the non-doped reactor and the LSC-PM in outdoor conditions (Fig. 4d and Supplementary Information). As highlighted in Fig. 2b, even with a high concentration of methylene blue in the channels, a significant portion of the luminescent photons escape the device through the light guide edges. To eliminate edge losses and retain the light within the light guide, we attached a reflective adhesive layer to the device’s four edges, de facto simulating an infinitely extended version of the corresponding designs. After preliminary tests on an interior window ledge, we moved the setup outdoors and performed the comparison between a 200 ppm LR305-doped LSC-PM and a non-doped reactor using solar irradiation on a partly sunny summer day with scattered cloud cover (average irradiation during the experiment: 323 W/m², see Supplementary Information for further details). Three different residence times (20, 15 and 10 seconds) were investigated for a period of half an hour each between 12:20 and 14:50 on July 7, 2016. In each case, the conversion in the dye-doped LSC-PM was significantly higher than in the non-doped reactor. For example, with a 10 seconds residence time the 30 minute averaged conversion was 96% for the LSC-PM versus 57% for the non-doped reactor. We noted that fluctuations in conversion due to the changes in cloud coverage were more attenuated in the LSC-PM than in the non-doped reactor where the performance was more erratic.

In summary, we pioneered a novel, leaf-inspired photomicroreactor that truly fulfills the sustainability premises of visible-light photoredox catalysis by using solar light as perennial energy source. Based on the luminescent solar concentrator concept, the device is capable of capturing direct and diffuse sunlight, converting it into a narrow wavelength and delivering it to the embedded microchannels. The performance of the device was studied both in indoor and outdoor conditions, significantly outperforming the non-dye-doped device. We believe that our strategy to merge flow photochemistry and luminescent solar concentrators represents a departure from the use of traditional solar photoreactors combined with reflectors and solar tracking modules. Also, we anticipate that the design will be applicable to other photochemical transformations, ultimately delivering a powerful tool for the sustainable and solar-driven continuous manufacturing of valuable chemical compounds, such as pharmaceuticals, agrochemicals and solar fuels.
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Figure 3 LSC-PM mediated wavelength conversion and light transport. (A) LSC-PM mediated wavelength conversion. Using blue LEDs as light source, the direct excitation of methylene blue (MB) is limited as evident by the low conversions obtained with the non-doped reactor (black squares). The fluorescent photons generated in the polymeric matrix are more likely to induce MB excitation, and therefore a dye-doping dependent increase in conversion is observed, proving the spectral conversion capabilities of the device. (B) To prove the light transport capabilities of the LSC-PM, a modified design was used where the reactor channels were situated in only half of the device. The half-device containing the reaction channel was covered with black cardboard, while the other half was orthogonally irradiated with a solar simulator. The doped designs resulted in significantly higher conversion rates as a result of the luminescent photons transporting the light energy throughout the device. (C) Complete comparison of non-doped and dye-doped reactors with simulated sunlight. The interpolation of the linear portion of the reaction kinetics indicates a 4.5-fold acceleration with the 200 ppm doped LSC-PM compared to the non-doped reactor (see Supplementary Information).

Figure 4 Solar light outdoor experiment. (A-C) 30-minute snapshots of the performance of a 200 ppm LR305 LSC-PM and a non-doped reactor on a partly sunny summer day with scattered cloud cover at different residence times (A 20 seconds, B 15 seconds, C 10 seconds). The average conversion in the 30-minute timeframe is reported along with the standard deviation. The LSC-PM is not only more efficient in gathering solar energy, but it is also more robust towards temporary variation of irradiation due to cloud coverage and scattering. (D) The experimental set-up employed for the solar experiment. (E) The two reactors employed in the experiment, with the reflectors on the edges.

Keywords
Photochemistry – Microreactors – Energy conversion – Luminescent solar concentrator – Solar energy

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29. The conversion in the non-doped reactor is mainly caused by the tailing of MB absorption spectrum in the 500 nm range. The molar extinction coefficient of MB at 500 nm is still 1500 M·cm⁻¹.
Artificial leaf for organic synthesis.
Herein, we propose a novel device integrating the luminescent solar concentrator (LSC) concept with photomicroreactors, allowing the efficient harvesting of solar light for use in photochemistry. This tree leaf-inspired photomicroreactor based on fluorescent dye-doped polydimethylsiloxane collects sunlight, focuses the energy to a narrow wavelength region, and then transports that energy to embedded microchannels where the flowing reactants are converted.

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