A Versatile Open-source Photoreactor Architecture for Photocatalysis Across the Visible Spectrum

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Supporting Information Placeholder

ABSTRACT: With the rapid growth of visible-light photocatalysis, many experimental strategies for conducting photoreactions have emerged. Several commercial photoreactors have been suggested as potential standards, but their adoption may be limited by high cost. Herein, we report the development of a versatile, open-source photoreactor platform that may prove to be suitable for general adoption. The "Wisconsin Photoreactor Platform" (WPP) utilizes inexpensive components in a 3D-printed enclosure and employs widely available high-intensity LEDs as the photon source. Physical dimensions and other features of WPP reactors can be readily varied to accommodate specific experimental goals, and new designs can be easily shared to facilitate transferability among laboratories. WPP performance is evaluated using six previously described transformations driven by light of disparate wavelengths.

Modern photocatalytic methods allow for formation of otherwise inaccessible products under mild conditions.[1] This capability has generated significant interest in the field of visible-light photocatalysis[2] and led many labs to explore incorporation of photocatalysis into their work.

Photochemical transformations can be significantly affected by small changes in experimental configuration.[3] The number of photons absorbed by the reaction mixture depends, in part, on the intensity and emission profile of the light source as well as the physical surroundings of the reaction vessel.[4] These factors make careful apparatus design and documentation essential for reproducible photoreaction outcomes and reliable reaction discovery.

A variety of approaches have been used to deliver photons to reaction vessels, but no single, standardized approach has seen widespread adoption to date.[4] Operational variation can hinder the reproduction of reported transformations, the description of which may include only minimal characterization of light source or description of experimental setup.[4,5] Entry of new researchers into this field and introduction of photoreactions into the chemistry curriculum should be facilitated by photoreactor platforms that enable accurate reproduction of the apparatus employed in a published study, facilitate apparatus customization for new applications in photocatalysis, and streamline the documentation of apparatus modifications. The work reported here is intended to achieve these goals.

Over the past few years, several commercial photoreactors designed to address problems outlined above have been reported.[3,5,6] More recently, an open-access 3D-printed enclosure for temperature-controlled photoreactions utilizing expensive commercial light emitting diode (LED) lamps was detailed by Schiel and coworkers.[7] These reactors integrate a rigid enclosure and exchangeable, high-power photon sources to improve reproducibility and reliability relative to ad hoc experimental setups. However, the adoption of these reactors as standards may be limited by their high cost. This problem is compounded by the significant cost of acquiring multiple proprietary photon sources when different emission profiles are required.[8]

Here we describe the Wisconsin Photoreactor Platform (WPP), an economical source of high-performance photoreactors that can be easily fabricated, readily modified and precisely documented (Figure 1). This platform provides reactors constructed from commercial components in a 3D-printed enclosure. The WPP is designed around inexpensive surface-mount LEDs as the light source. All design files are open-source to maximize transferability. A specific reactor with bespoke physical parameters can be fabricated by an experimentalist with no prior experience in less than a day (instruction in supporting information). The WPP is modular and allows photoreactor capabilities to be expanded by use of a well-established array of compatible electronic peripherals. These factors combine to provide a versatile architecture that could contribute to the standardization of photochemical protocols and enhance the discovery and optimization of new photochemical reactivity.

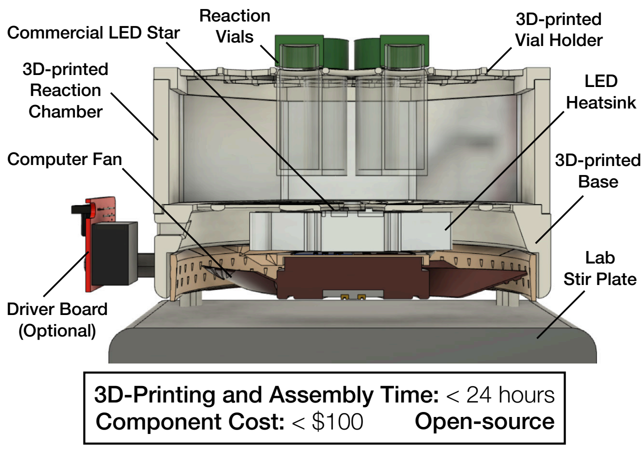

Figure 1. 3D Cutaway view of the Wisconsin Photoreactor Platform architecture with labeled components. Estimated component cost is in US dollars as of 2021.

We viewed the photon source as the most important component of the WPP. An ideal source would be limited to the wavelength range necessary to drive an intended transformation. Sources that emit light in a narrow wavelength range minimize undesired heating and side reactions.[9] Therefore, we were drawn to single-color LEDs rather than broadly emitting light sources, such as compact fluorescent lights (CFL) (Figure 2A). High-intensity LEDs with narrow emission profiles across the visible range are available in inexpensive commercial packages (Figure 2B-C). Access to defined but diverse photon sources is important for new reaction discovery, as demonstrated by recent reports of red and near-infrared (NIR) light photocatalysts.[10,11] Commercial high-intensity LEDs have seen use in several recent studies of photocatalysis.[12]

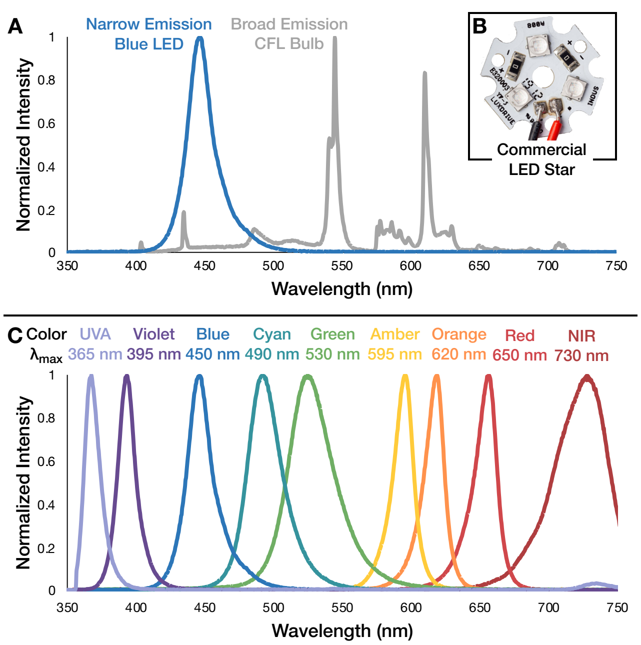

Figure 2. (A) Comparison of emission spectra of 450 nm Cree, Inc. XT-E Royal Blue LED and ALZO Digital full spectrum CFL bulb. (B) Industry-standard LED star mounted with 450 nm Cree, Inc. XT-E LEDs. (C) Emission spectra of commercial LEDs purchased from manufacturers Cree, Inc., Luxeon and Inolux.

A 3D-printed enclosure was designed to house a LED star and multiple reaction vials (Figure 3A). As shown in Figure 1, this enclosure is composed of a compact base, a reaction chamber and a vial holder. These three components fit together rigidly, which ensures reproducibility of reaction vessel placement relative to the photon source. Chambers and vial holders with different physical parameters can be designed, printed and exchanged with one another, which allows the experimentalist to use a variety of vessels. These designs can be documented in research publications to facilitate transferability to other laboratories. We provide printable modules for various common reaction vessels in the supporting information.

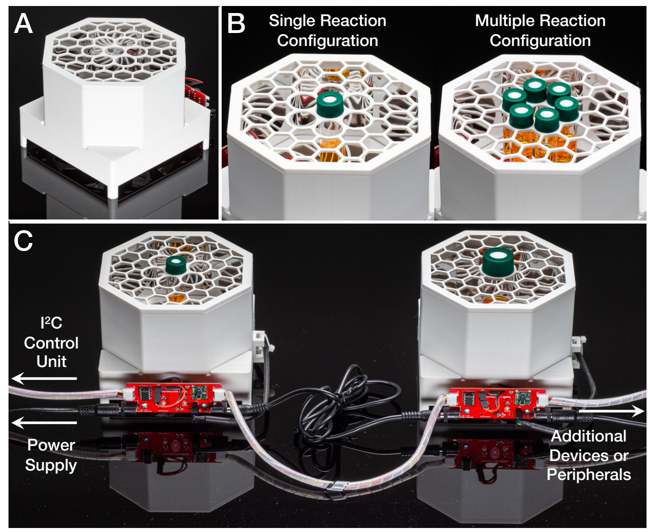

Figure 3. (A) Assembled WPP device. B) Single and multiple reaction configurations of a WPP device fitted with a 4 mL vial holder and reaction chamber module. (D) Illustration of WPP expandability using optional driver circuit boards.

The vial holders we have designed can illuminate several vials equally, for rapid screening of experimental variables, or a single vial, for greatest light exposure (Figure 3B). The photoreactor incorporates a commercial aluminum heatsink and low-profile computer fan to cool the LED and reaction vessels. Standard lab stir plates can be used with the small-footprint WPP architecture.

To support kinetics studies or screening of reaction conditions, we designed a custom driver board to control operation of multiple WPP devices simultaneously. Reactors fitted with these boards can be connected in-series to a single power source and control unit (Figure 3C). The control unit can then "supervise" the light intensity and fan speed of each WPR via I^2C, a commonly used protocol for communication among digital integrated circuits.[13] If extended functionality is needed, any I^2C-compatible peripherals could be connected to the driver board for use with the WPP architecture. Many I^2C-compatible devices and sensors are commercially available, including thermocouple adapters for temperature monitoring.[14] For work not requiring such control and expandability, a standard 1000 mA LED driver can be used. A driver board offering control over light intensity using a simple potentiometer is described in the supporting information.

Our intention is to make the WPP architecture suitable as an open standard, with specific reactors easily producible by any chemist. Toward that end, we have included our enclosure and electronics design files as well as detailed component sourcing

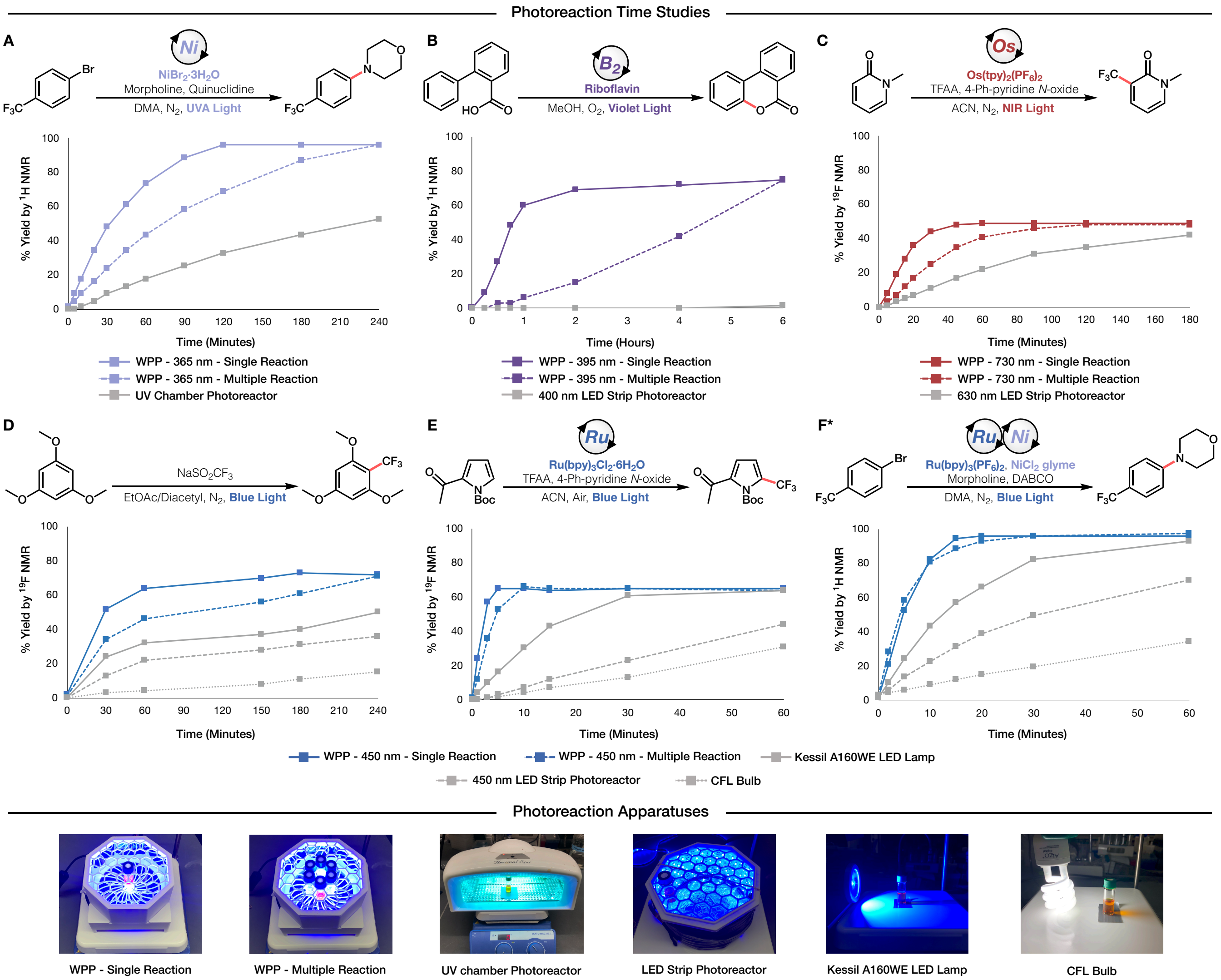

Figure 4. Time studies of six literature photochemical reactions illustrating performance of WPP platform relative to typical experimental setups. All reactions were conducted in 4 mL vials with ca. 1 to 2.5 mL of reaction volume. For exact conditions and procedures, see the supporting information. Yields were determined by ^{1}H or ^{19}F NMR analysis of crude reaction mixtures using mesitylene or trifluorotoluene as an internal standard. (*) The "WPP – 450 nm – Single Reaction" benchmark was conducted in a 4 °C refrigerator at 90% light intensity.

and fabrication instructions in the supporting information. A "living" online repository to which users can contribute custom WPP modules is provided.[15] 3D-printers and 3D-printing services are readily available. We have found that the enclosure can be fabricated using a variety of affordable 3D-printers. Commercial small-scale printed circuit board fabrication is inexpensive and widely available. Our driver boards can be assembled quickly without specialized tools. These features should encourage adoption of the WPP.

To establish the versatility and reliability of the WPP architecture relative to typical experimental setups, we applied this approach to six reactions from the recent photocatalysis literature that are driven by light of disparate wavelengths. Photoreaction apparatuses used for comparison were derived from setups reported in the literature (see supporting information). WPP device performance across both the single reaction and multiple reaction configurations shown in Figure 3B was evaluated.

In presenting the results in Figures 4 and 5, we do not mean to imply that the WPP is the best way to conduct any particular photochemical reaction. Instead, we offer these data to suggest that use of the WPP platform is likely to provide good results for a wide range of photochemical transformations. In addition, because the specifics of a WPP device can be easily varied and documented, results achieved with this approach can be readily reproduced in other laboratories. These features may be particularly useful for researchers seeking to initiate studies in this important field.

The first "benchmark" process was the C-N cross-coupling of 4-bromobenzotrifluoroide and morpholine via the photoexcitation of nickel-amine complexes with ultraviolet A (UVA) light, as described by Miyake et al. (Figure 4A).[12a] In both single- and multiple-reaction configurations, a WPP device fitted with a 365 nm LED star decreased reaction time relative to a more conventional apparatus fashioned from a commercial UV light curing chamber.[16] With the WPP approach, reaction completion was reached in 2 or 4 hours with 96% yield for the single- or multi-reaction configuration, respectively. The UV chamber achieved only 53% yield after 4 hours of illumination.

Synthesis of 3,4-benzocoumarin using violet light and the vitamin photocatalysis strategy detailed by Gilmour et al. was examined next (Figure 4B).[12b] Using a standard 400 nm LED strip reactor, based on the design of Stephenson et al.,[17] we obtained < 5% yield after 8 hours of continuous illumination. In contrast, a WPP device with a 395 nm light source provided 75% yield across single- and multi-reaction configurations after 8 hours, indicating the robust performance of the WPP architecture in this transformation. The single-reaction configuration achieved 72% yield after only 2 hours.

Inspired by the recent report of Rovis et al. on the development of NIR photocatalysts,[11] we examined their Os-photocatalyzed trifluoromethylation of *N*-methyl-2-pyridone using a WPP device with a 730 nm LED star (Figure 4C). Both WPP configurations provided faster product formation than did a 630 nm LED strip photoreactor, despite stronger absorption of the $Os(tpy)_2(PF_6)_2$ photocatalyst at 630 nm.[11] The trifluoromethylated product was generated in 48% yield with both WPP configurations after 2 hours of illumination, while the LED strip reactor provided 35% yield.

We explored reactor efficacy with three blue light photoreactions previously used by MacMillan et al. to benchmark a commercial photoreactor.[3] We first tested our platform's performance in catalyzing the trifluoromethylation of 1,3,5-trimethoxybenzene using the method reported by Li and coworkers (Figured 4D).[18] A WPP device with 450 nm LEDs yielded product faster and in higher yield than did conventional experimental setups involving a Kessil A160WE LED lamp, a 450 nm LED strip reactor or a CFL bulb. Six reactions of this type simultaneously carried out using a WPP device in the multiple reaction configuration exhibited a consistent reaction profile, indicating the reliability of the WPP architecture (Figure S22 in supporting information). The same trend was observed when the protocol of Stephenson et al. for trifluoromethylation of 2-acetyl-*N*-Boc pyrrole was evaluated (Figure 4E).[19] Finally, the metallophotoredox-catalyzed C-N cross coupling of bromobenzotrifluoride and morpholine of MacMillan et al. revealed a similar trend (Figure 4F).[20] Across all three blue-light reactions, both WPP configurations offered superior performance relative to the conventional experimental setups tested.

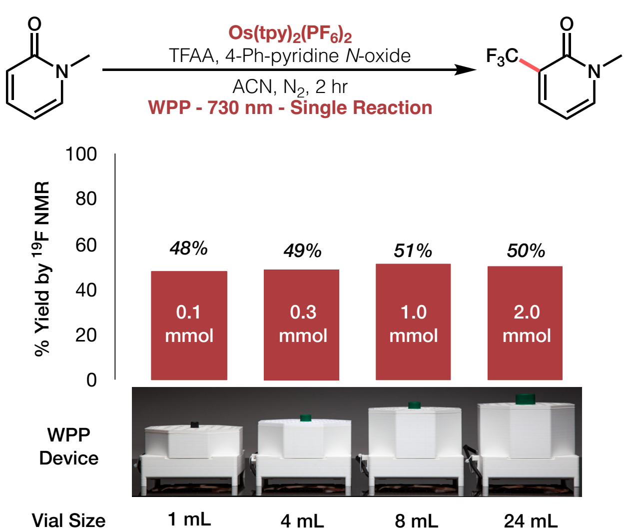

Figure 5. Results of scale-up trials. Reactions conducted at indicated scales using listed reaction vessel sizes. Yields were determined by ^{19}F NMR analysis of crude reaction mixtures using trifluorotoluene as an internal standard.

As an additional test of architecture generality, we evaluated WPP performance across a series of typical laboratory reaction scales (Figure 5). Using the photocatalytic trifluoromethylation of *N*-methyl-2-pyridone as a testbed, we conducted reactions at 0.1, 0.3, 1.0 and 2.0 mmol scale in a WPP device fitted with a 730 nm LED star. Enclosure modules for each scale were designed to standardize reaction vessel placement across all trials. In all cases, product was generated in ca. 50% yield after 2 hours. Increases in reaction scale up to 20-fold relative to the initial 0.1 mmol trial reaction were accommodated without loss of performance.

We have developed an open-source photoreactor platform that enables rapid progress in cutting-edge photocatalysis research and has a low barrier for adoption. The Wisconsin Photoreactor Platform is inexpensive, adaptable and highly featured; therefore, the WPP should foster standardized experimental protocols and reproducibility. We have demonstrated the favorable performance of WPP devices across a series of benchmark photoreactions using UVA, violet, NIR and blue light as well as in reaction scale-up. The WPP architecture meets the need for a standardized approach to experimental apparatus that is versatile, reliable, can be precisely documented and easily reproduced, and is economically accessible to a broad community of researchers.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

Photon source characterization data, experimental details and NMR spectra (PDF)

Wisconsin Photoreactor Platform apparatus bill of materials, fabrication instructions and operation guide (PDF)

Wisconsin Photoreactor Platform project repository (zip)

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ACKNOWLEDGMENT

We thank Prof. Tehshik Yoon and Prof. AJ Boydston for helpful discussions. We are grateful to Dr. Ilia Guzei for photography, the Weix and Stahl labs for sharing reagents and the Goldsmith group for use of an Ocean Insight spectrometer. We thank Sebastian Thompson for help in fabrication of custom LED stars and organic chemistry lab teaching staff for donation of a UV light chamber. This research was supported in part by the US National Science Foundation (CHE-1904940). Spectroscopic instrumentation was supported by the UW Madison Instructional Laboratory Modernization Award and NIH grant 1S10 OD020022-1.

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(15) Users of the WPP can contribute custom modules, electronics and other designs to the WPP repository for others to use. See: https://github.com/uw-madison-chem-shops/wisconsin-photoreactor

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