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# **Supporting Information**

# **Cloud-Inspired Multiple Scattering for Light Intensified Photochemical Flow Reactors**

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**Keywords:** visible-light flow photochemistry • light absorption intensification • multiple scattering • packed glass bead flow reactor

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## I. Photochemical Reactions in Single Phase Reactor and Packed

## **Bed Reactor**

#### 1. Single phase reactor

A syringe pump (Harvard PHD 2000 series) was used to deliver the starting solution into the reactor tube (5 mm ID PFA). The residence time is determined by the total reactor volume divide by the flow rate. Thus, the tube length and flow rate were adjusted to control the residence time for reaction. A blue or black LED stripe was wrapped into a cylindrical shape where the reactor tube passes through the center and light was received radially by the tube. The reaction sample was collected. After that, the sample was subjected to GC analysis and/or crude NMR analysis.

#### 2. Packed bed reactor

The glass beads (d =  $\sim$ 75 µm, acid washed) were packed in 7 cm of 1 mm PFA tubing, 1.8 cm of 5 mm PFA tubing and 2.7 cm of 10 mm PFA tubing. The stainless-steel beads (d =  $\sim$ 67-78 µm) were packed in 7 cm of 1 mm PFA tubing. The corresponding mass loading of glass beads was 40, 260, 1560 mg respectively, with a liquid volume per unit length of 2, 50, 200  $\Box$ L/cm respectively. Residence times were calculated by dividing the free volume within the reactor (determined by the bead size and total mass used) by the liquid flow rates. Thus, the flow rate is adjusted to tune the residence time for reaction in this reactor. The methods for illumination, sample collection and sample analysis are same as the single-phase reactor. A back-pressure regulator (40 psi) was used for the 5/10 mm reactors to achieve steady flow

distribution. In all cases. aluminium foil was used to protect the supply syringe and the inlet and outlet sections of the tubing from illuminated by the LED light source, thus ensuring that the photochemical reaction took place only in the reactors.



Figure S1. (a) Schematic of the experimental setup for photocatalysis conducted in this study. (b) Photograph of the actual setup of the experiment. The entire setup (cylinder with LED strip) was wrapped with aluminium foil throughout the reaction.(c) Photograph of the 10 mm packed reactor.



**Figure S2**. Reactor performance comparison for a visible-light-promoted E/Z isomerization

# II. Measurement of the Molar Extinction Coefficient of the Reaction Medium

The catalyst  $(Ir(ppy)_3)$  used for photochemical Z-alkene synthesis was dissolved in DCE. Subsequently, the reaction vessel was deoxygenated by sparging with nitrogen for 10 minutes (as described above). A series of different concentrations of the Ir(ppy)\_3 solution (80 - 300  $\square$ M) were placed in a quartz cuvette and used for UV-Vis absorbance measurement, using a Shimadzu UV-1800 UV-Vis spectrophotometer. The molar extinction coefficient ( $\varepsilon$ ) of the reaction medium can be estimated based on Beer-Lambert law, knowing the absorbance (A), concentration (c) and light path length (l) inside the cuvette. After obtaining  $\square$   $\square$  by tuning the complex part of the reaction medium refractive index in the COMSOL model, we can match the absorbance simulated for a 1 mm ID single phase reactor in COMSOL with Beer's law predicted absorbance for the same reactor based on the experimentally determined  $\square$ . Hence obtain the corresponding complex part of refractive index value for the system.

# **III. COMSOL Simulation**

The three-dimensional ray tracing was conducted with Geometrical Optics interface in a commercial finite-element solver (COMSOL Multiphysics), where every ray was traced individually. The iterative solver GMRES was selected with a relative convergence tolerance of  $10^{-5}$ . Incident rays with initial intensity of  $381[W/m^2]$  at 470 nm for photocatalytic E-to-Z isomerization and 450 nm for dual photoredox and nickel catalysis reaction (metallaphotoredox-catalyzed amination) were used in the simulation, and their propagation in the fluid between the glass-fluid interfaces was explicitly studied for each ray until it reached its intensity threshold limit of 1e- ${}^{3}$ [W/m<sup>2</sup>]. The refractive index of glass beads was 1.52, and of the reaction medium was 1.445 for photocatalytic E-to-Z isomerization and 1.477 for dual photoredox and nickel catalysis reaction. In addition, the projected plane grid was used for initial ray position with 100 rays. Initial unpolarized rays and surface curvature wavefront shape were used. The incident rays were propagated in the x-axis direction at the start of the simulation. To complete the whole simulation, 1348 time steps were chosen with an interval of 9.61e-15 s per time step for 2.5 mm x 0.98 mm x 0.38 mm representative volume (5 mm ID reactor cases) and 2599 time steps with an interval of 1.08e-14 s per time step for 5.0 mm x 0.98 mm x 0.38 mm representative volume (10 mm ID glass bead reactor case). Specular reflection wall conditions were set for all surfaces of the representative volume except for the surfaces parallel to the Y-Z plane (Figure 3 in main text). The output power of rays leaving the Geometrical Domain at last time step, from YZ-plane, was evaluated with Accumulated Variables under Geometrical

Optics.



**Figure S3**. Ray-tracing for photocatalytic E-to-Z isomerization reaction using glass beads. Reflected rays are omitted here for better visualization and only refracted rays are shown.



**Figure S4**. Ray-tracing for photocatalytic E-to-Z isomerization reaction using singlephase. There are no secondary rays in this case.

# **IV. General Information**

Chemicals and anhydrous solvents were purchased from commercial suppliers and used as received. Trans- $\beta$ -methylstyrene (99%), tris[2-phenylpyridinato-C<sup>2</sup>, N [iridium(III) [Ir(ppy)<sub>3</sub>]] (99%), N, N-diisopropylethylamine (DIPEA) (>99%), 4bromobenzotrifluoride (99%), pyrrolidine (99%), Ir[dF(CF<sub>3</sub>)ppy]<sub>2</sub>(dtbpy))PF<sub>6</sub>, nickel(II) bromide ethylene glycol dimethyl ether complex NiBr<sub>2</sub>•DME (97%), 1,4diazabicyclo[2.2.2]octane (DABCO) (>99%), dimethyl sulfoxide (>99.9%), tetramethylethylene (99%), 2-benzylidenemalononitrile (98%), 9-mesityl-10methylacridinium perchlorate Mes-Acr<sup>+</sup> ClO<sub>4</sub><sup>-</sup> (95%), tetrahydrofuran (anhydrous,  $\geq$ 99.9%), anthraquinone (97%), and 1,2-dichloroethane (99.8%) were purchased from Sigma Aldrich and used as received. Diethyl ether (≥99.7%) was purchased from VWR and used as received. Glass beads (size 75 µm, acid-washed) were purchased from Sigma Aldrich. All GC analysis was performed on Shidmadzu 2010Plus. <sup>1</sup>H NMR spectra were recorded on a Bruker AV-III400 (400 MHZ) or AMX500 (500 MHz) spectrometer. UV-Vis absorbance measurement was conducted using a Shimadzu UV-1800 UV-Vis spectrophotometer. The Blue LED strips (2 meter, 18 W) and UV-A LED stripes (2 meter, 18 W) were purchased from Inwares Pte Ltd (Singapore). For some reactions, lower light powers were used by covering the LED strips by aluminum foil partially.



Figure S5. Emission spectrum of blue LED strips (maximum emission at around 470 nm).



Figure S6. Emission spectrum of UV-A LED strips (maximum emission at around 395 nm).

# **V. General Procedure for Photochemical Reactions**

#### 1. Photochemical synthesis of Z-Alkene

To an oven-dried vial was added Ir(ppy)<sub>3</sub> (20 mg, 0.015 equiv) and 20 mL of DCE, followed by addition of trans- $\Box$ -methylstyrene (260 µL, 2 mmol, 1.0 equiv) and DIPEA (36 µL, 0.2 mmol, 0.1 equiv). Subsequently, the reaction vessel was placed in an ice bath and deoxygenated by sparging with nitrogen for 10 minutes. The mixture was sonicated for 10 min and then attached to the corresponding flow apparatus with 5W (electric power) blue LED irradiation. The reaction yield was determined by GC analysis of reaction mixture using 1,3,5-trimethylbenzene as an internal standard and verified by crude <sup>1</sup>H NMR. The molar extinction coefficient of Ir(ppy)<sub>3</sub> at the wavelength of 470 nm, which was determined experimentally using a UV-Vis absorbance measurement, is 1700 M<sup>-1</sup>cm<sup>-1</sup>.



Figure S7. Typical GC analysis for photochemical synthesis of Z-Alkene



Figure S8. Typical crude <sup>1</sup>H NMR analysis for photochemical synthesis of Z-Alkene.

#### 2. Metallaphotoredox-catalyzed amination

To an oven-dried vial was added DABCO (1.367g, 12.22 mmol, 1.8 equiv),  $(Ir[dF(CF_3)ppy]_2(dtbpy))PF_6$  (5.7 mg, 0.0007 equiv), NiBr<sub>2</sub>•DME (104.6 mg, 0.05 equiv) and 25 mL of dimethyl sulfoxide, followed by addition of 4-bromobenzotrifluoride (950 µL, 6.783 mmol, 1.0 equiv) and pyrrolidine (850 µL, 10.18 mmol, 1.5 equiv). Subsequently, the reaction vessel was deoxygenated by sparging with nitrogen for 10 minutes. The mixture was sonicated for 10 min and then attached to the corresponding flow apparatus with 5W (electric power) blue LED irradiation. The reaction yield was determined by GC analysis of reaction mixture using dodecane as an internal standard, and it was verified by crude <sup>1</sup>H NMR using

1,3,5-trimethoxybenzene .as an internal standard. The molar extinction coefficient of  $(Ir[dF(CF_3)ppy]_2(dtbpy))PF_6$  at the wavelength of 450 nm is 567 M<sup>-1</sup>cm<sup>-1</sup>.<sup>[1]</sup>



Figure S9. Typical GC analysis for metallaphotoredox-catalyzed amination.



**Figure S10.** Typical crude <sup>1</sup>H NMR analysis for metallaphotoredox-catalyzed amination.

### 3. Photoredox-catalyzed allylic alkylation

To an oven-dried vial was added 2-benzylidenemalononitrile (30.8 mg, 0.2 mmol, 1.0 equiv), 9-mesityl-10-methylacridinium perchlorate (8 mg, 0.05 equiv) and 20 mL of anhydrous DCE, followed by addition of tetramethylethylene (400  $\Box$ L, 3.2 mmol, 16.0 equiv). Subsequently, the reaction vessel was placed in an ice bath and deoxygenated by sparging with nitrogen for 10 minutes. The mixture was sonicated for 10 min and then attached to the corresponding flow apparatus with 18W (electric power) blue LED irradiation. The reaction yield was determined by GC analysis of reaction mixture using dodecane as an internal standard, and it was verified by crude

<sup>1</sup>H NMR using 1,3,5-trimethoxybenzene as an internal standard. The molar extinction coefficient of 9-mesityl-10-methylacridinium perchlorate at the wavelength of 500 nm is 5500 M<sup>-1</sup>cm<sup>-1</sup>.<sup>[2]</sup>



Figure S11. Typical GC analysis for photoredox-catalyzed allylic alkylation.



**Figure S12.** Typical crude <sup>1</sup>H NMR analysis for photoredox-catalyzed allylic alkylation.

#### 4. Photo-mediated C-H alkylation via hydrogen atom transfer

To an oven-dried vial was added 2-benzylidenemalononitrile (15.5 mg, 0.1 mmol, 1.0 equiv) and anthraquinone (3.2 mg, 0.2 equiv) and 25 mL of anhydrous tetrahydrofuran. Subsequently, the reaction vessel was placed in an ice bath and deoxygenated by sparging with nitrogen for 10 minutes. The mixture was sonicated for 10 min and then attached to the corresponding flow apparatus with 9W (electric

power) UV-A LED irradiation. The reaction yield was determined by GC analysis of reaction mixture using dodecane as an internal standard, and it was verified by crude <sup>1</sup>H NMR using 1,3,5-trimethoxybenzene as an internal standard. The molar extinction coefficient of anthraquinone at the wavelength of 390 nm is 10200 M<sup>-1</sup>cm<sup>-1</sup>.<sup>[3]</sup>



Figure S13. Typical GC analysis for photo-mediated C-H alkylation via hydrogen atom transfer.



**Figure S14**. Typical crude <sup>1</sup>H NMR analysis for photo-mediated C-H alkylation via hydrogen atom transfer.

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