Electronic Supplementary Information

Titanium Dioxide Visible Light Photocatalysis: Surface Association Enables Diels-Alder Photocatalysis with Visible Light Irradiation

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A. General Information

Indole was purchased from Fisher Scientific and purified by recrystallization from hexanes before use. 1,3-Cyclohexadiene was purchased from Fisher Scientific and purified by distillation in the presence of $NaBH_4$ before use. Acetyl chloride was purchased from Sigma Aldrich and purified by distillation in the presence of *N,N*-dimethylaniline before use. $MeNO_2$ was purchased from Sigma Aldrich, was purified by drying over $CaCl_2$ and distilling, and was then stored under an argon atmosphere. The TiO_2 P25 employed was provided as a gift from Nippon Aerosil Co., Ltd (Batch #: 4168091398) and used as received. All LEDs employed in this work were purchased from LedEngin. Flash column chromatography was performed using 230-400 mesh silica gel. All ^1H and ^{13}C were recorded on either a Bruker AVANCE 400 (400 MHz) or a Bruker AVANCE III (500 MHz) spectrometer. Chemical shifts (δ) are reported in ppm from the solvent resonance as the internal standard ($CDCl_3$: δ 7.26 ppm). UV-Vis spectra were recorded using an Agilant Cary 7000 Spectrophotometer, and diffuse reflectance spectra were recorded using an Agilant Cary 100 Spectrophotometer.

B. Example Procedure for the Photocatalytic Diels-Alder Reaction

To an oven dried 10 mL Schlenk tube was added indole (0.3 mmol, 35 mg), TiO_2 (12 mg), and $NaHCO_3$ (0.6 mmol, 50 mg). The vessel was then charged with $MeNO_2$ (3 mL), and freshly distilled 1,3-cyclohexadiene (1.5 mmol, ~150 μL) and acetyl chloride (0.3 mmol, 21 μL) were added. The reaction mixture was then sonicated until the TiO_2 catalyst was completely dispersed. The reaction was then irradiated with a 10 W 460 nm LED for 5 h. Following irradiation, the reaction was transferred into a 15 mL centrifuge tube and centrifuged at 3,000 rpm for 15 min. The supernatant was then transferred to a round bottomed flask, and the solvent was evaporated under reduced pressure.

The product was isolated as individual isomers by purifying the crude reaction mixture by flash column chromatography (4:1 Hexanes:EtOAc), yielding the known title compound as a colorless oil (52 mg (*Endo* + *Exo*), 72% isolated yield). *Endo:Exo* ratio was determined by ^1H NMR analysis of the crude reaction mixture before purification and was calculated to be 3.6:1.

C. Spectral Data for *N*-Acetyl-1,4,4a,9a-tetrahydro-1,4-ethanocarbazole

Endo Isomer:

^{1}H NMR: (500 MHz, $CDCl_3$) δ 8.11 (d, *J*=7.93 Hz, 1 H), 7.19-7.07 (m, 2 H), 7.03-6.94 (m, 1H), 6.09-6.01 (m, 1H), 5.96-5.83 (m, 1H), 4.65 (d, *J*=7.93 Hz) and 4.40 (dd, *J*=9.31,2.29 Hz) (1 H, two rotamers), 3.69 (dd, *J*=9.16 Hz) and 3.53 (d, *J*=8.85 Hz) (1 H, two rotamers), 3.39 (br. s), 3.10-2.83 (m) (2 H, two rotamers), 2.39 (s) and 2.31 (s) (3 H, two rotamers), 1.76-1.59 (m, 2H), 1.46-1.24(m, 2H).

^{13}C NMR: (101 MHz, DMSO-d_6) δ 168.71, 144.47, 134.78, 134.24, 130.17, 126.69, 123.66, 123.09, 115.73, 63.37, 45.69, 34.23, 33.44, 23.45, 23.13, 21.95.

Reference: *J. Org. Chem.*, 1991, **56**, 1405-1411.

Exo Isomer:

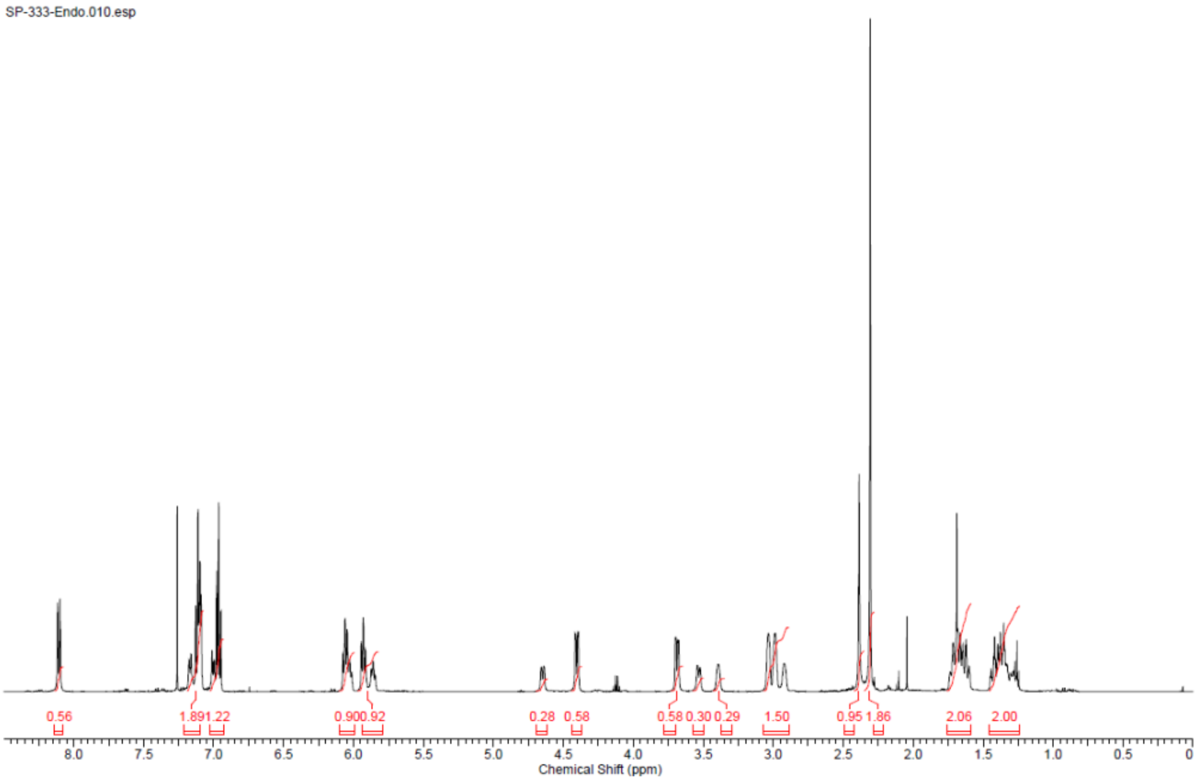
^{1}H NMR: (500 MHz, $CDCl_3$) δ 8.24 (d, *J*=8.24 Hz, 1H), 7.25-7.19 (m, 1H), 7.19-7.07 (m, 1H), 7.06-7.01 (m, 1H), 6.61-6.46 (m, 1H), 6.39-6.27 (m, 1H), 4.55-4.47 (m) and 4.26 (dd, *J*=10.68, 1.22 Hz) (1 H, two rotamers), 3.54 (dd, *J*=10.68, 3.36 Hz) and 3.44-3.37 (m) (1 H, two rotamers), 3.30 (br. s) and 2.97-2.77 (m) (2 H, two rotamers), 2.46 (s) and 2.28 (s) (3 H, two rotamers), 1.61-1.38 (m, 1H), 1.33-1.21 (m, 1H), 1.17-0.96 (m, 2H).

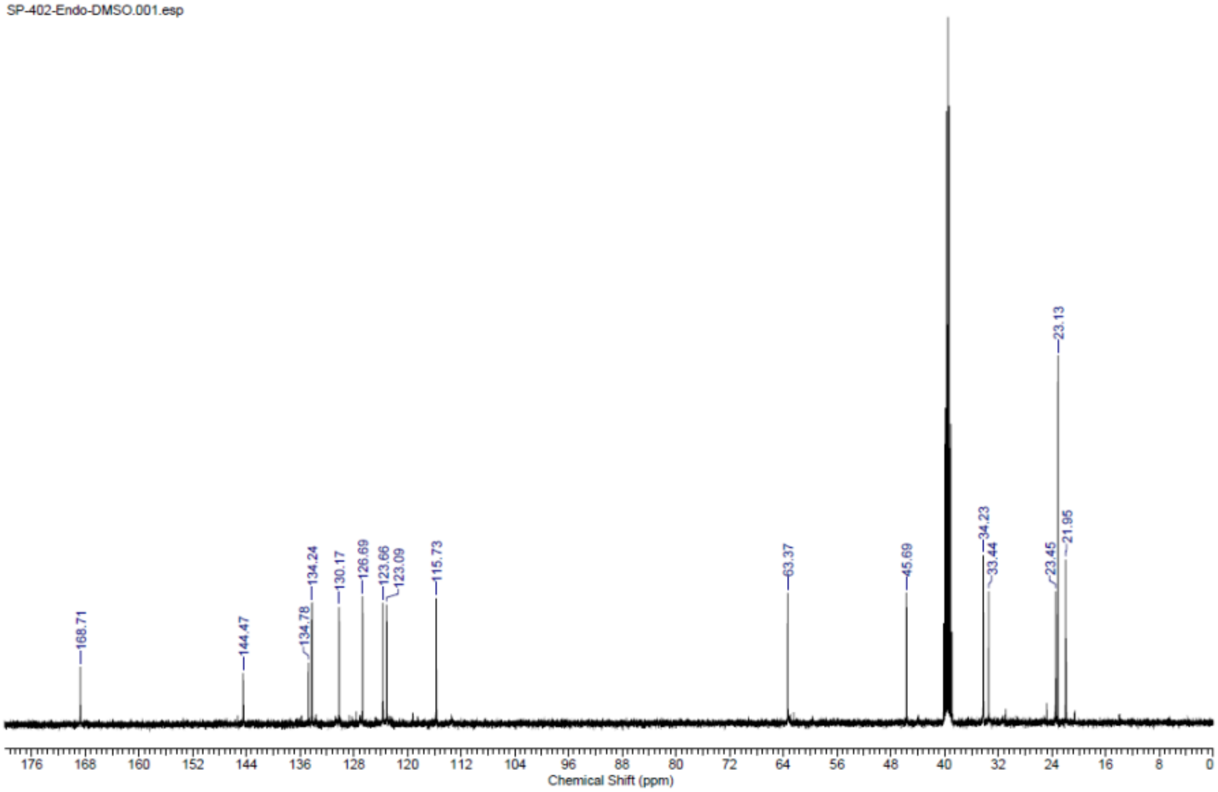
^{13}C NMR (101 MHz, DMSO-d_6) δ 169.20, 144.30, 136.63, 132.68, 132.20, 127.44, 124.47, 123.32, 116.41, 63.01, 42.80, 33.21, 32.50, 23.40, 20.96, 16.86.

Reference: *J. Org. Chem.*, 1991, **56**, 1405-1411.

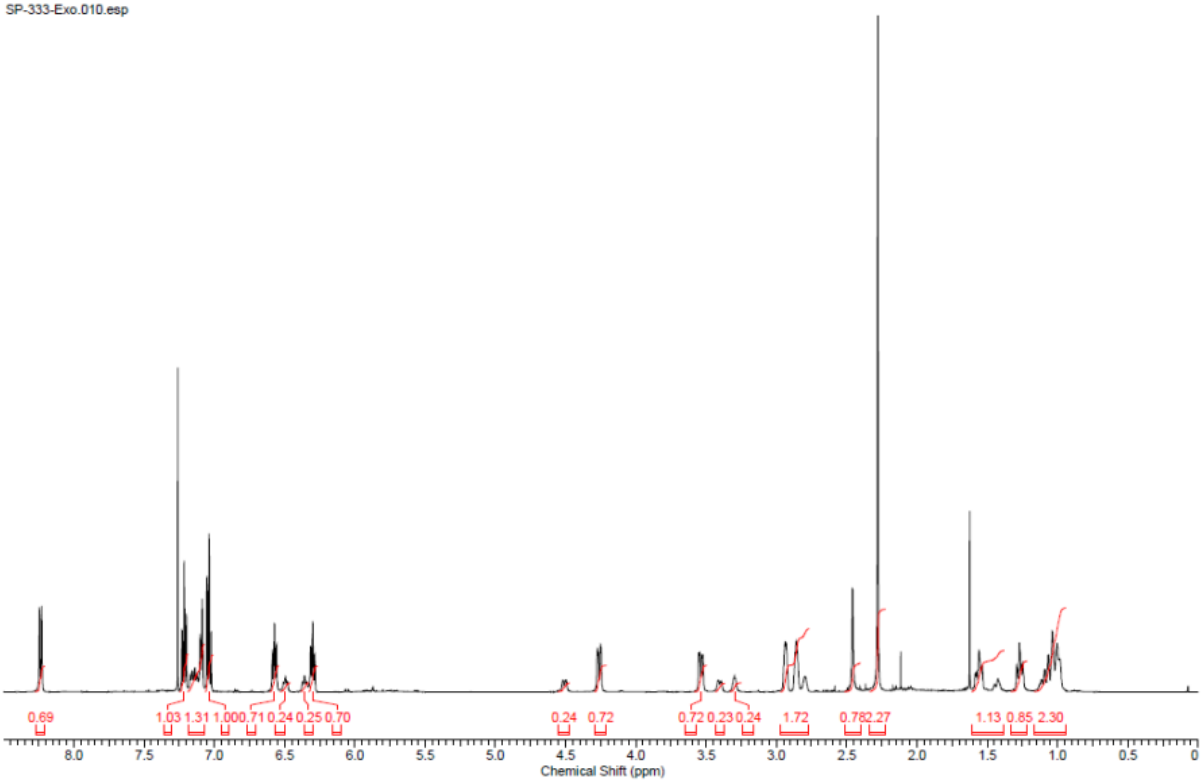
NMR Spectra

Endo Isomer





Exo Isomer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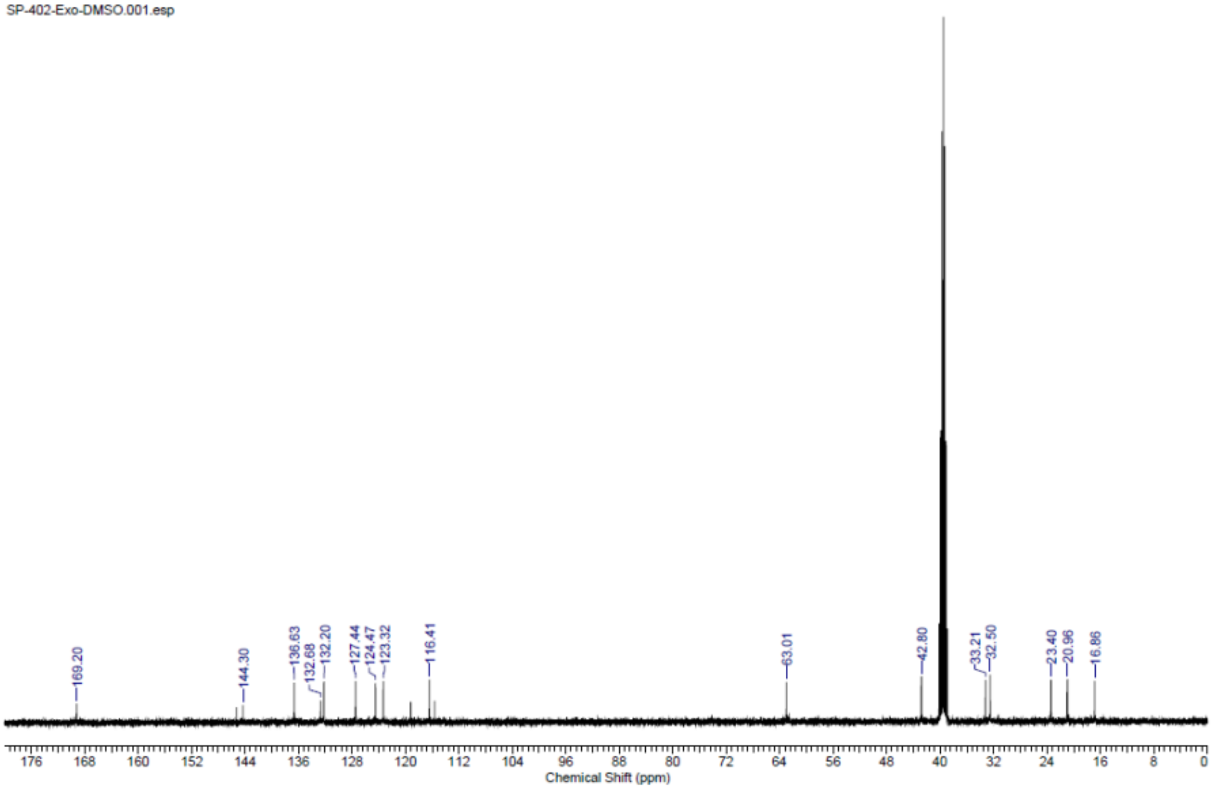
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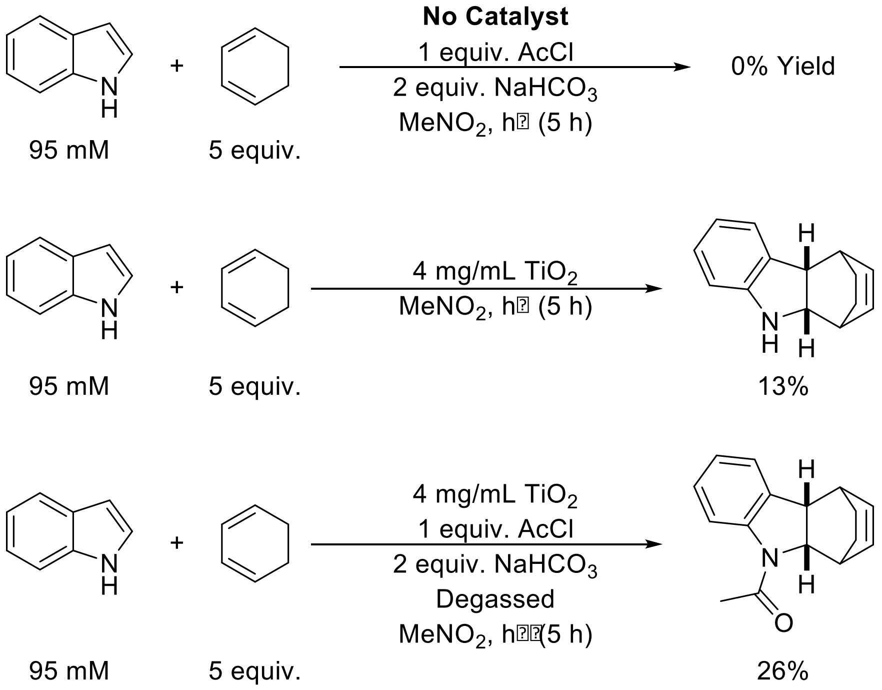
Chemical Shift (ppm)

D. Control Reactions



Scheme S1. Control reactions for the photocatalyzed Diels-Alder reaction of indole and 1,3-cyclohexadiene mediated by TiO_2.

E. TiO_2 Diffuse Reflectance Before and After Photocatalysis

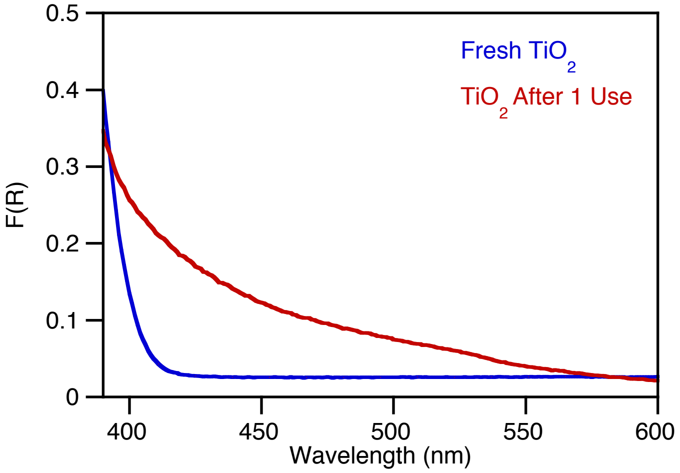


Figure S1. Diffuse reflectance spectra of fresh TiO_2 (blue), and TiO_2 which was recovered by centrifugation after the reaction (red).

F. FTIR Spectra

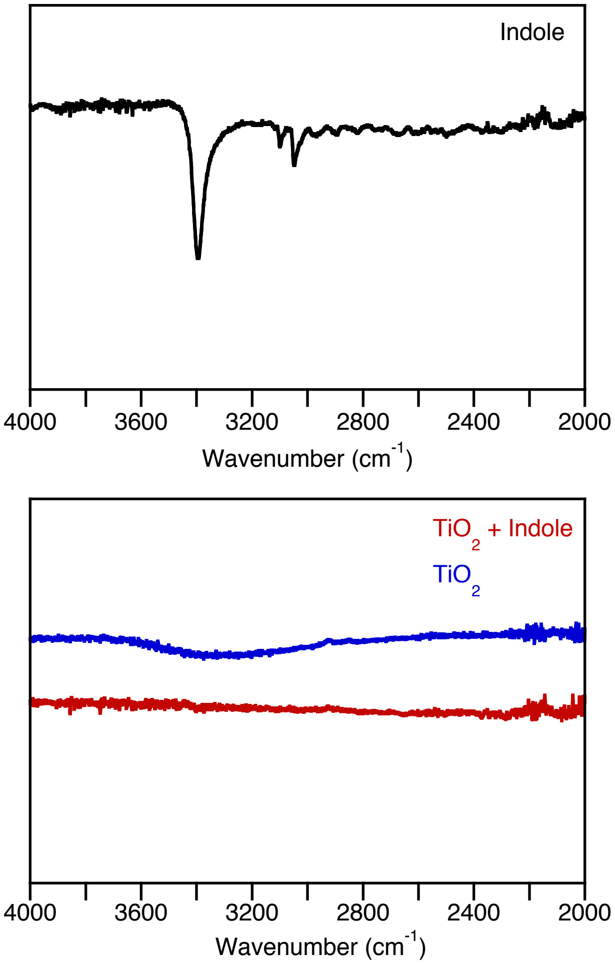


Figure S2. FTIR spectra of indole (black), TiO_2 (blue), and TiO_2 that was exposed to a 100 mM solution of indole (red). The disappearance of the N-H stretch in the TiO_2-indole sample indicates adsorption of indole occurs through dissociation.

G. 10 W 460 nm LED Set Up and Emission Spectrum

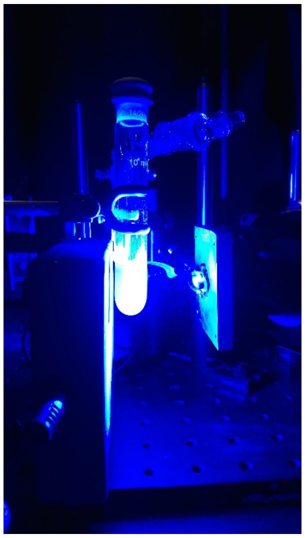


Figure S3. Picture of LED set up used for the photocatalytic Diels-Alder reactions.

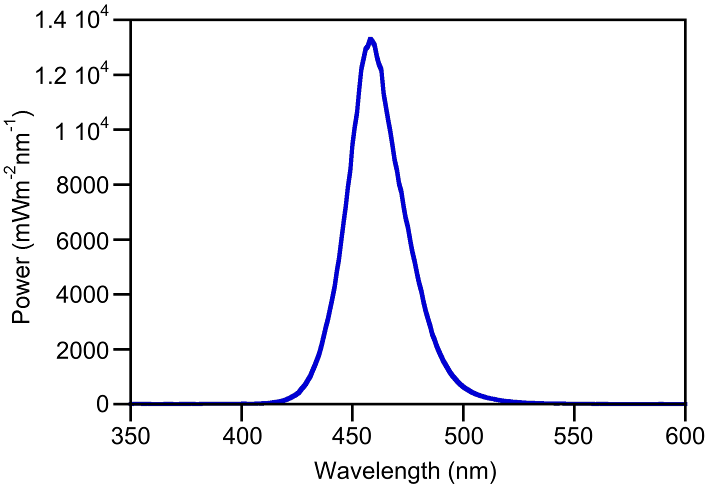


Figure S4. Emission spectrum for the 10 W 460 nm LED utilized for the photocatalytic Diels-Alder reactions.

H. Experimental Set Up for the Action Spectrum Experiments

In order to perform the action spectrum for our photocatalytic Diels-Alder reaction, we needed to design a set up in which we could calculate the photon flux delivered by each LED. The simplest method was to employ a spectroradiometer to measure the output of the LED (in W/m^2). Using the spectroradiometer, each LED was set to a total output power of 30 W/m^2, and using the equations outlined in the manuscript, the mole of photons being delivered from the LED per unit time was calculated.

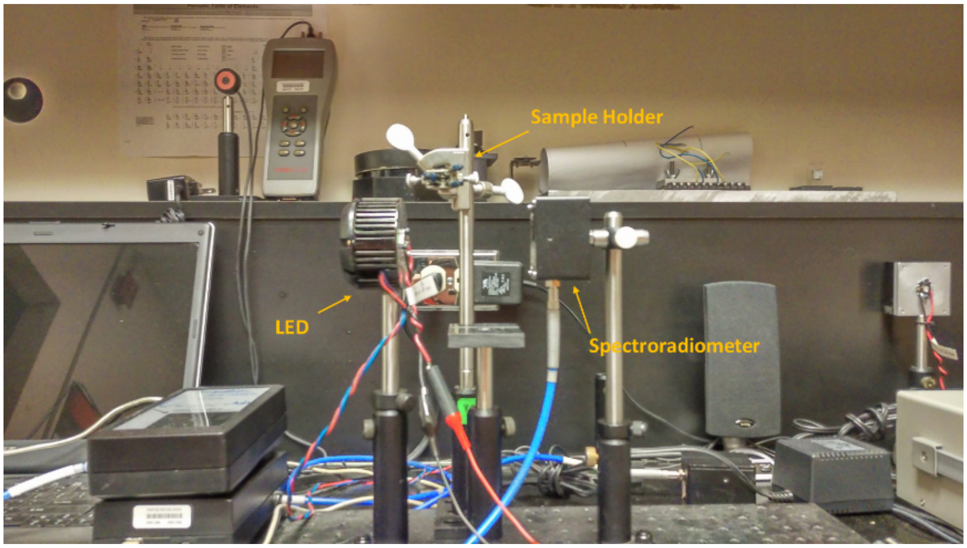


Figure S5. Photograph of the experimental set up employed for the action spectrum experiments.

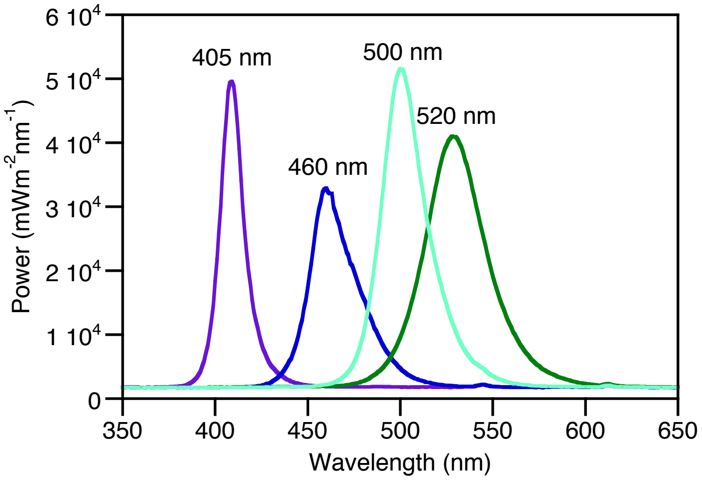


Figure S6. Emission spectrum for LEDs utilized for the action spectrum measurements.