



### Additional UC Synthesis Information

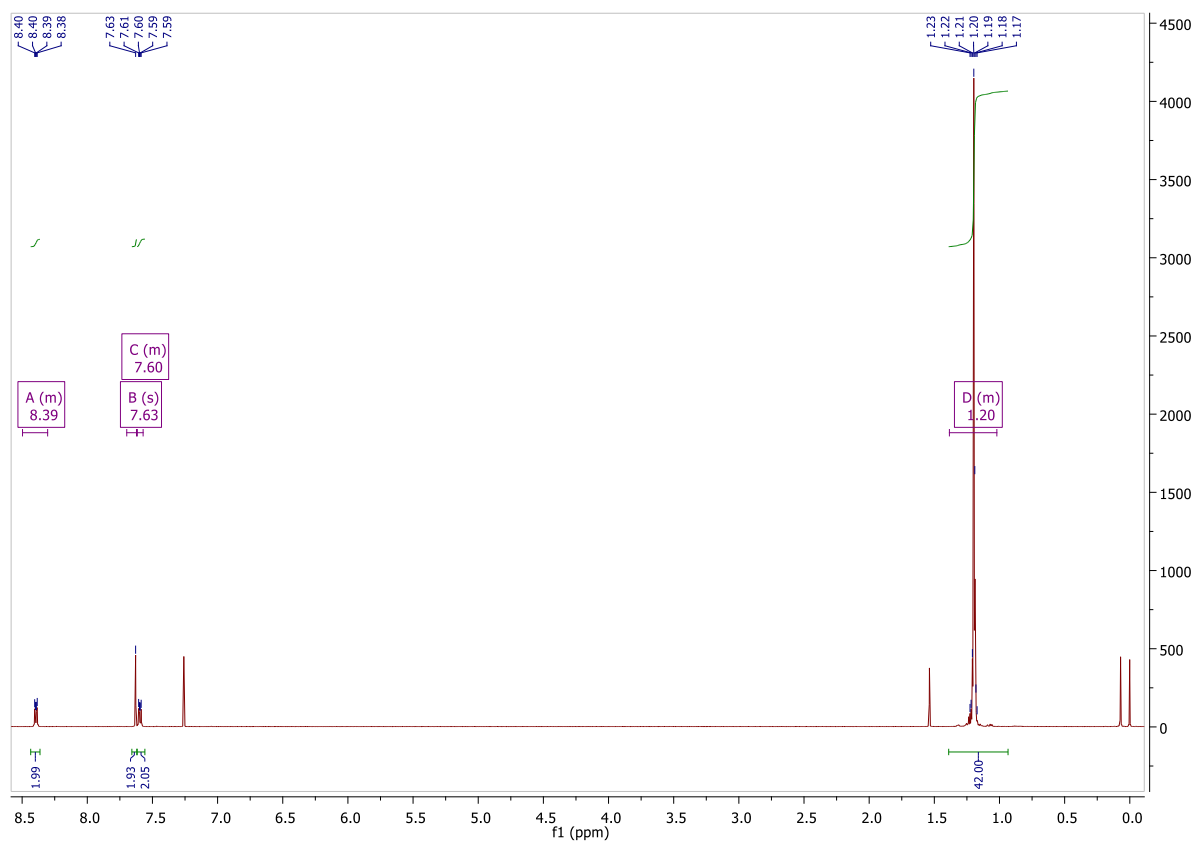
All chemicals used in the synthesis of the upconversion material were purchased from Merck. NMR spectra were obtained using an Agilent DD2 500 MHz spectrometer. HRMS spectra were obtained using an Agilent 6230 TOF LC/MS.

The synthesis of TIPS-naphthalene (TIPS-Nph) was adapted from Harada et al.<sup>1</sup> A mixture of 1,4-dibromonaphthalene (1.44g, 5.03 mmoles), Pd (PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (80.65 mg, 114.58 mmoles), CuI (60.89 mg, 319.72 mmoles), and PPh<sub>3</sub> (82.34 mg, 313.93 mmoles) were dissolved with stirring in 40 mL THF under an argon atmosphere, to which diisopropylamine (36 mL, 256.86 mmoles) was added. The reaction mixture was heated to 100°C and (triisopropylsilyl)acetylene (3.5294 g, 19.35 mmoles) was added dropwise over 5 minutes via addition funnel. The mixture was then stirred at 100°C for 10 hours, cooled to room-temperature, and concentrated *in vacuo*. The concentrated mixture was dissolved in chloroform, dried over Na<sub>2</sub>SO<sub>4</sub>, filtered, and then concentrated by rotovap to give crude TIPS-naphthalene as a black crystalline solid. This crude product (Rf: 0.6, blue fluorescent) was then purified by chromatography using a 6 cm I.D. silica gel column and n-hexane as the eluent. The fractions containing the desired product were concentrated by rotovap to give a white powder. The white powder was recrystallized from methanol (~300 mL) to give 1.4416g TIPS-naphthalene as a white crystalline solid (59% yield, mp 94.5-95.4 °C). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, TMS): δ: 8.39 (m, 2H), 7.63 (s, 2H), 7.60 (m, 2H), 1.17-1.23 (m, 42H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>, TMS): δ: 135.85, 132.77, 129.80, 129.25, 124.41, 107.40, 100.43, 21.41, 14.05. HRMS (ESI) (*m/z*) calculated for [C<sub>32</sub>H<sub>48</sub>Si<sub>2</sub>]<sup>+</sup>: 488.3290, found: 488.3301.

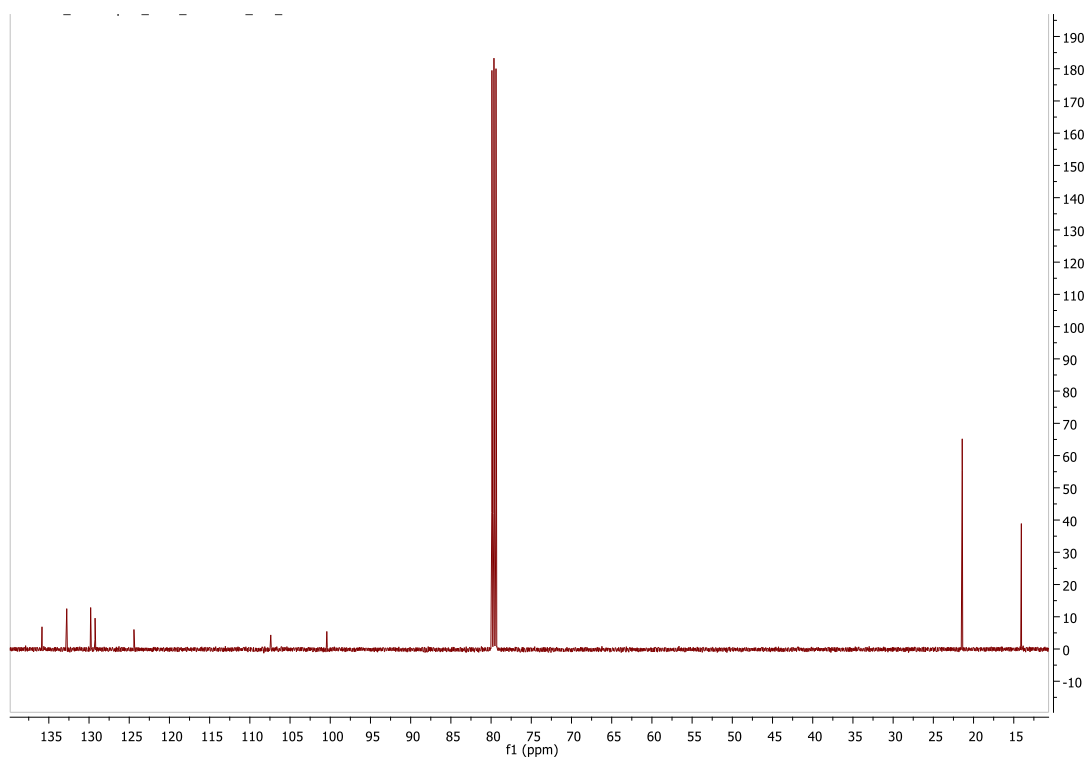
The synthetic procedure used for the synthesis of Ir(C6)<sub>2</sub> was adapted from: Borisov and Klimant<sup>2</sup>, Lamansky et al.<sup>3</sup>, DeRosa et al.<sup>4</sup>, and Nonoyama.<sup>5</sup> Coumarin 6, abbreviated C6, (1.2075 g, 3.45 mmoles) was added to a solution of Ir(III) chloride hydrate (0.5046 g, 1.69 mmoles) in a solution of 2-ethoxyethanol and water (3:1, 40 mL). The reaction mixture was stirred at room temperature for 8 hours and then refluxed for 24 hours at 124°C, to give a dark red/brown mixture with a light orange precipitate. The orange precipitate was collected by filtration, rinsed with ethanol, then dried in a desiccator to give [Ir(C6)<sub>2</sub>Cl]<sub>2</sub> (1.0240 g, 0.88 mmoles). The chloro-bridged dimer [Ir(C6)<sub>2</sub>Cl]<sub>2</sub> was then added to a mixture of acetylacetonone (0.5492 g, 5.48 mmoles), Na<sub>2</sub>CO<sub>3</sub> (0.8204 g, 7.74 mmoles) in 2-ethoxyethanol (60 mL), the resultant mixture was stirred for 10 hours at 120 °C under N<sub>2</sub> atmosphere. The crude product was cooled to room temperature and then concentrated at 57 °C under vacuum to give a dark orange/red crude powder. The crude powder was then purified by silica gel column using 1:1 CH<sub>2</sub>Cl<sub>2</sub>: ethyl-acetate as the eluent to give a yellow/orange powder came out near the sand layer, this powder was dissolved with CH<sub>2</sub>Cl<sub>2</sub> and collected. The collected solution was concentrated *in vacuo* and then further dried under vacuum for 24 hours, to give Ir(C6)<sub>2</sub>(acac) as an orange powder (0.4881 g, 45%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, TMS): δ: 7.88 (d, 2H, *J* = 7.9 Hz), 7.60

(d, 2H,  $J = 8.3$  Hz), 7.30 (t, 2H,  $J = 7.5$  Hz), 7.23 (t, 2H,  $J = 7.7$  Hz), 6.29 (d, 2H,  $J = 2.3$  Hz), 6.07 (d, 2H,  $J = 9.2$  Hz), 5.84 (dd, 2H,  $J = 9.2$  Hz, 2.3 Hz), 4.87 (s, 1H), 3.15-3.28 (m, 8H), 1.71 (s, 6H), 1.04 (t, 12H,  $J = 7.0$  Hz). HRMS (ESI) ( $m/z$ ) calculated for  $[\text{C}_{45}\text{H}_{41}\text{IrN}_4\text{O}_6\text{S}_2]^+$ : 990.2108, found: 990.2155.

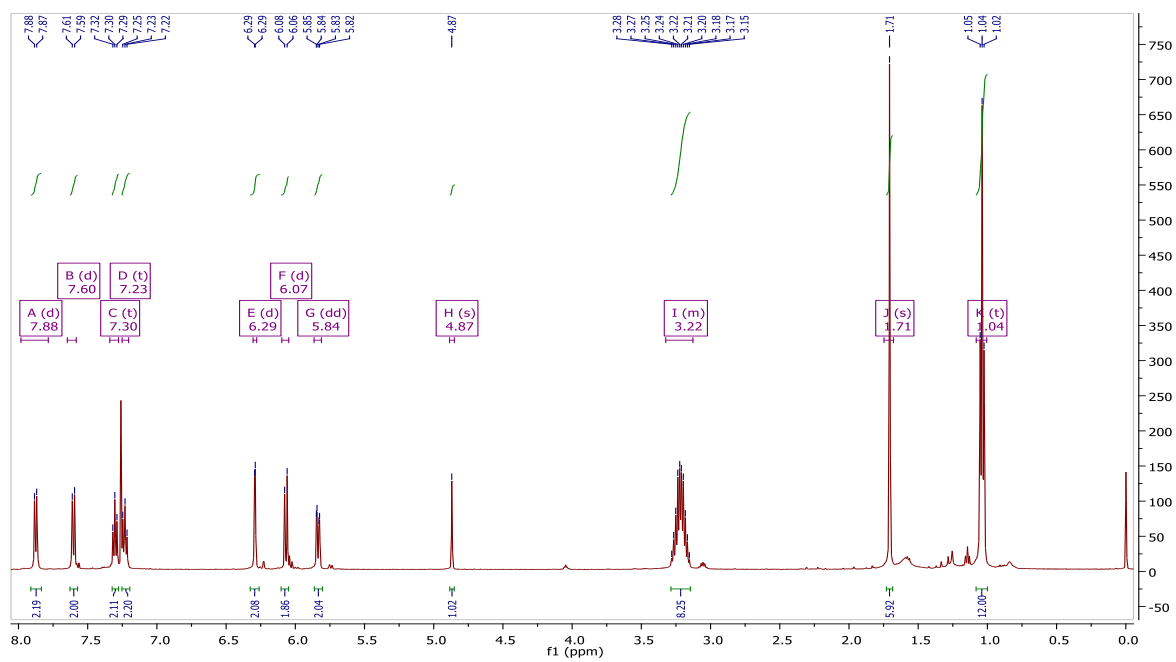
### $^1\text{H}$ NMR spectrum of TIPS-naphthalene



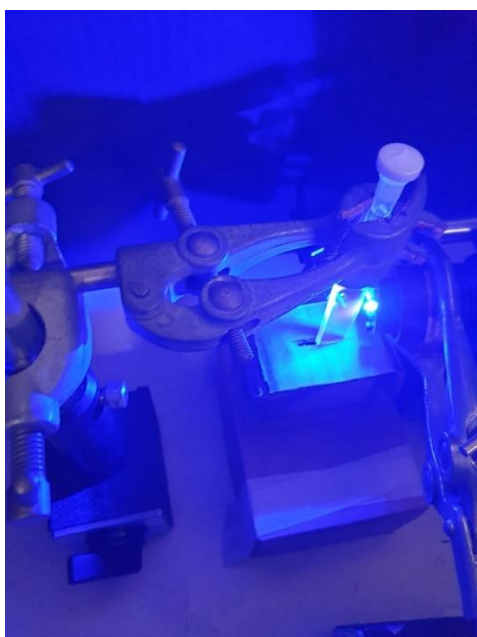
### $^{13}\text{C}$ NMR spectrum of TIPS-naphthalene



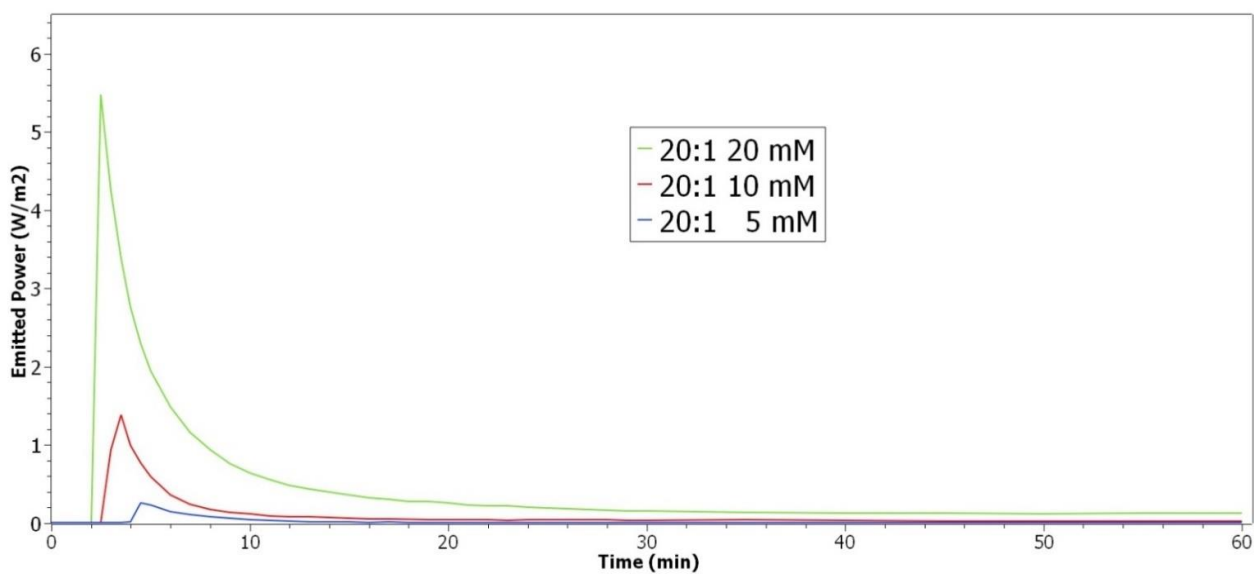
### $^1\text{H}$ NMR spectrum of Ir(C6)<sub>2</sub>(acac)



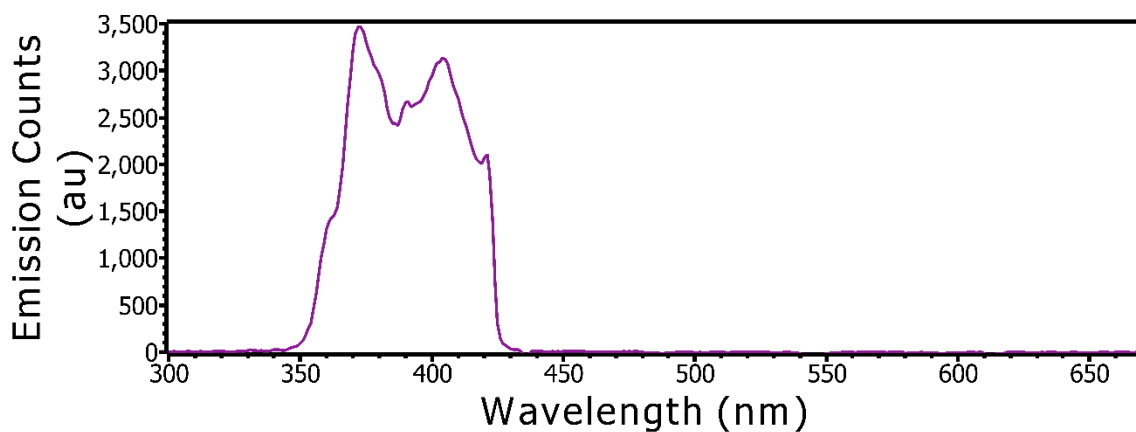
## Additional Figures for the TTA-UC System



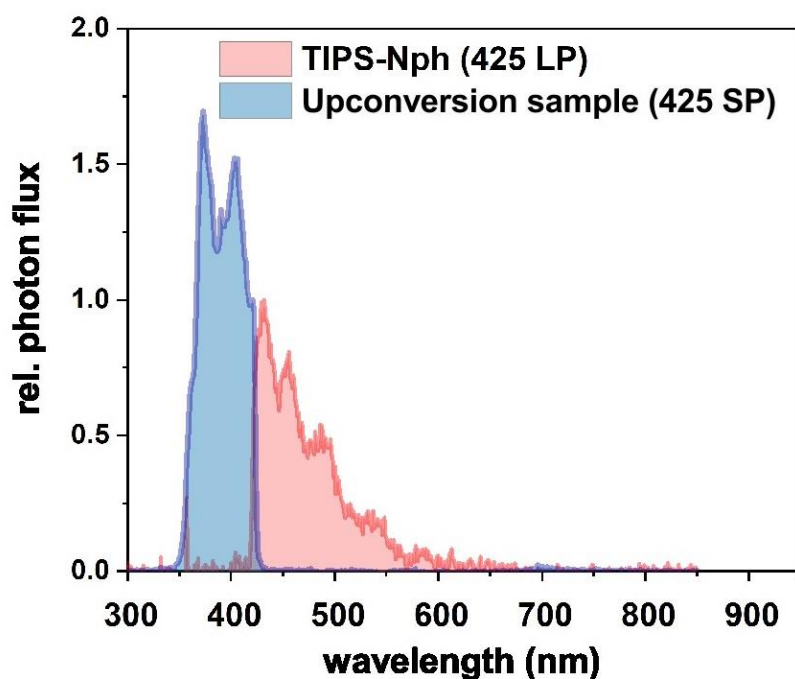
**Figure S1:** Spectrometer enclosure (University of Adelaide) showing the cuvette containing UC material being irradiated with the 455 nm LED, and optical fibre placed at 90° connecting to the spectroradiometer.



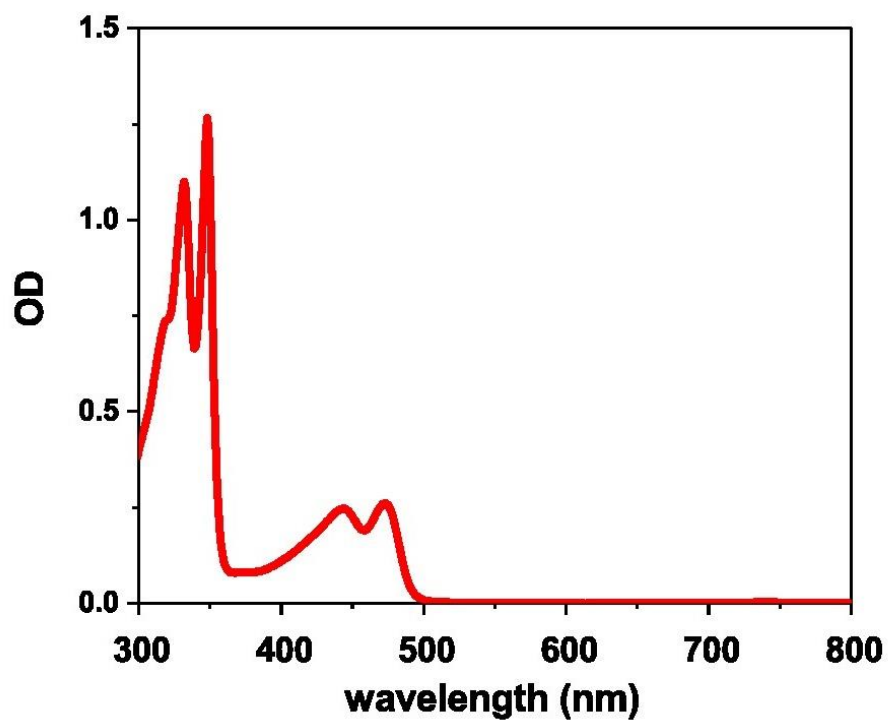
**Figure S2:** Upconversion power decay over 1 hour for three different concentrations of emitter, as measured with the spectroradiometer (University of Adelaide).



**Figure S3:** Steady-state upconverted emission spectra of TIPS-Ir sample excited at 450 nm and measured with a 425 nm short pass filter.



**Figure S4:** Emission spectrum of UC sample (excited with a 450 nm laser and measured with a 425 nm short-pass filter) and the emission spectrum of TIPS-Nph (excited with a 405 nm laser and measured with a 425 nm long pass filter), normalised to the peak at 425 nm (at UNSW).



**Figure S5:** UV-Vis absorption spectrum of Ir(C6)<sub>2</sub>(acac) (recorded at UNSW).

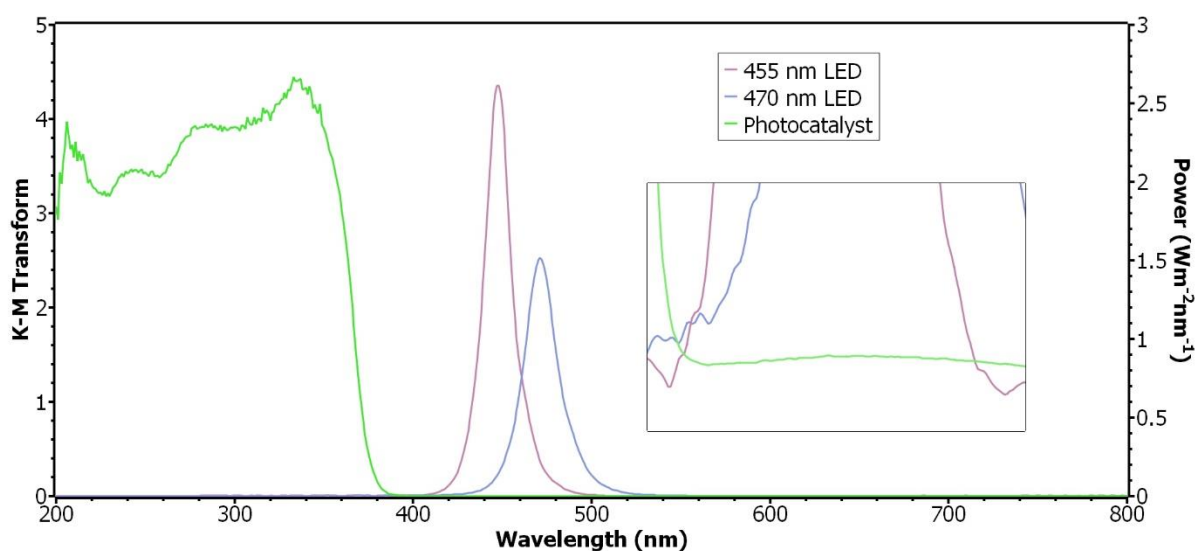
#### **Additional Photocatalysis Information**



**Figure S6:** Photocatalysis reactor cell set-up; filling the photocatalyst, adding the water, and performing the purge by bubbling Ar through a needle.

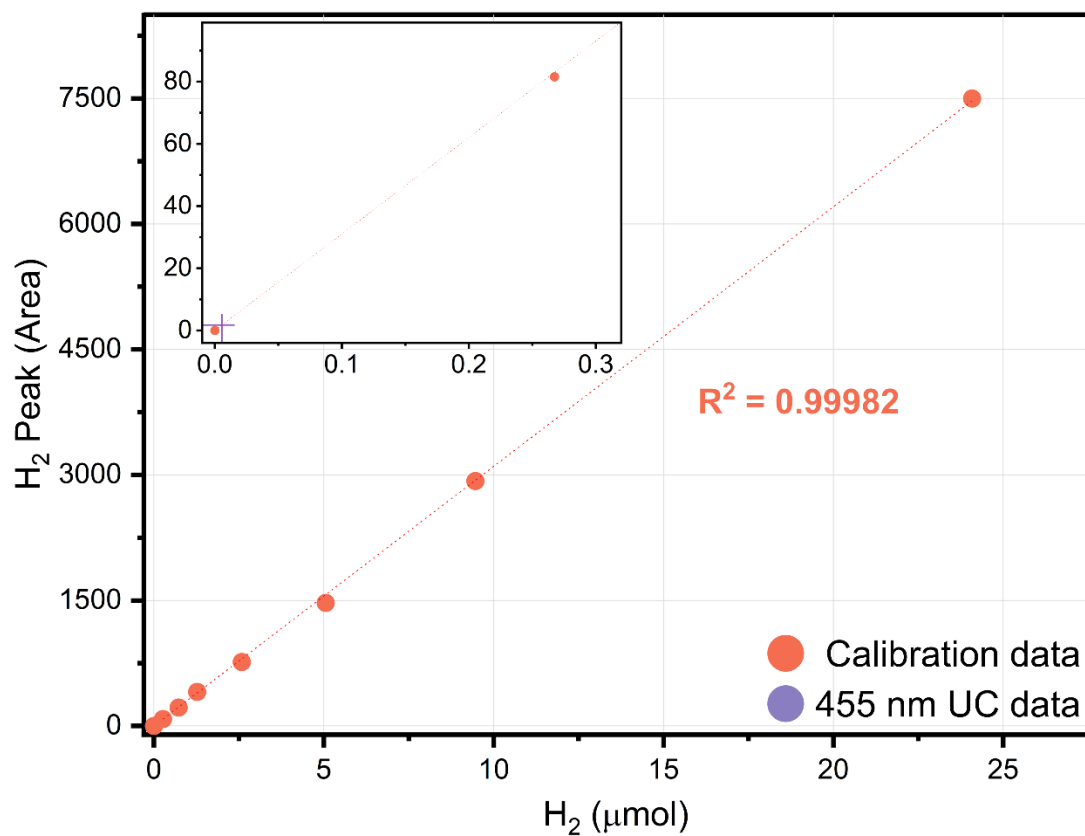


**Figure S7:** Photo showing the photocatalysis reactor in operation under 455 nm LED illumination. The metal support ensures the cuvettes containing the UC material and the photocatalyst material close together.

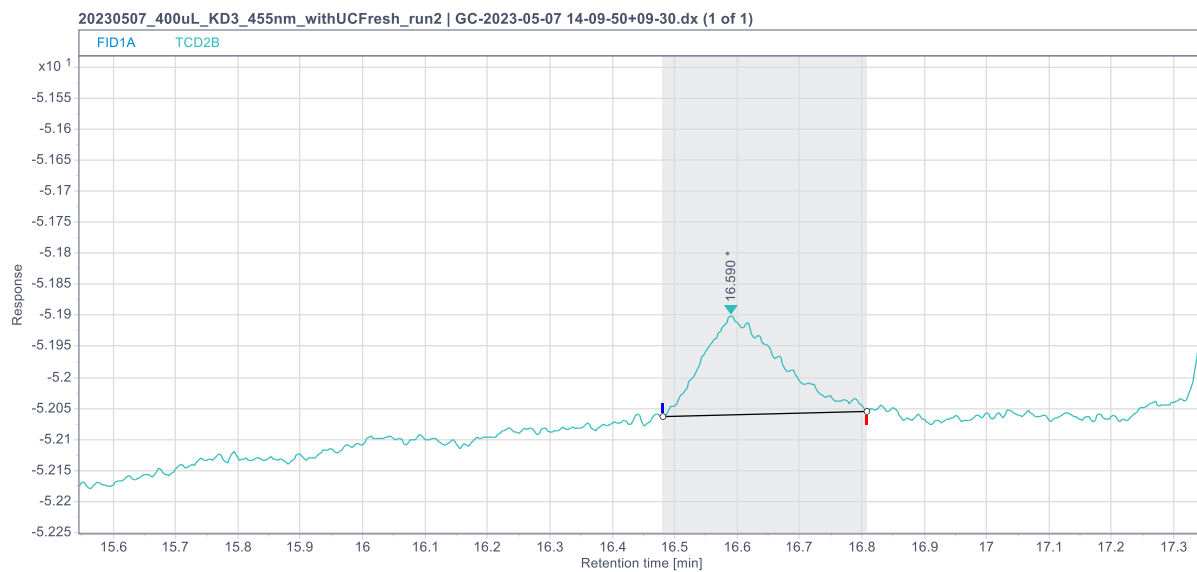


**Figure S8:** DRS of the Al:STO (left hand axis) photocatalyst and the emitted power of the 455 and 470 nm LEDs (right hand axis). The inset shows the very slight overlap of the photocatalyst absorption at both LED wavelengths which gives rise to the background H<sub>2</sub> signal.





**Figure S9:** H<sub>2</sub> Calibration plot demonstrating a strong linear trend from 0 μmol to 24.08 μmol. The inset depicts a zoomed-in version showing the first two calibration points and the intercept corresponding to the observed UC 455 nm peak areas in the GC-MS.



**Figure S10:** Example trace of the GC-MS, showing a clear peak at the H<sub>2</sub> retention time of 16.6 min.

## Sample AQY Calculation

The following information is taken from Table 2:

	455 nm (control)	455 nm (UC)
$\mu\text{mol H}_2$	0.00332	0.00537
No. photons	$2.88 \times 10^{17}$	

1. Determine  $\mu\text{mol H}_2$

$$(0.00537 \mu\text{mol}) - (0.00332 \mu\text{mol}) = 0.00205 \mu\text{mol}$$

2. Determine in number of  $\text{H}_2/\text{s}$  from our  $\text{H}_2$  in 10 min

$$\frac{(0.00205 \mu\text{mol}) \times \left(\frac{6.022 \times 10^{23} \text{ molecules H}_2}{10^6 \mu\text{mol}}\right)}{600 \text{ s}} = 2.1 \times 10^{12} \text{ molecules H}_2 \text{ s}^{-1}$$

3. Getting %AQY accounting for stoichiometry and no. photons

$$\frac{2 \times (2.1 \times 10^{12} \text{ molecules H}_2 \text{ s}^{-1})}{(2.88 \times 10^{17} \text{ photons})} \times 100 = 1.43 \times 10^{-3}\%$$

## Additional References

- 1 Harada, N., Sasaki, Y., Hosoyamada, M., Kimizuka, N. & Yanai, N. Discovery of key tips-naphthalene for efficient visible-to-uv photon upconversion under sunlight and room light. *Angew Chem Int Ed Engl* **60**, 142-147, doi:10.1002/anie.202012419 (2021).
- 2 Borisov, S. M. & Klimant, I. Ultrabright oxygen optodes based on cyclometalated iridium(III) coumarin complexes. *Analytical Chemistry* **79**, 7501-7509, doi:10.1021/ac0710836 (2007).
- 3 Lamansky, S. *et al.* Synthesis and characterization of phosphorescent cyclometalated iridium complexes. *Inorganic Chemistry* **40**, 1704-1711, doi:10.1021/ic0008969 (2001).
- 4 Derosa, M. C. *et al.* Iridium luminophore complexes for unimolecular oxygen sensors. *Journal of the American Chemical Society* **126**, 7619-7626, doi:10.1021/ja049872h (2004).
- 5 Nonoyama, M. Benzo[h]quinolin-10-yl-N Iridium(III) complexes. *Bulletin of the Chemical Society of Japan* **47**, 767-768, doi:10.1246/bcsj.47.767 (1974).