

Electronic Supplementary Information

**Direct photo-hydroxylation of the Zr-based framework
UiO-66**

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1. Materials

Zirconium chloride ($ZrCl_4$), terephthalic acid (bdc), hydroxyterephthalic acid (OH-bdc), TiO_2 (Aeroxide P25), ethylene glycol, sodium acetate (NaAc), polyethylene glycol (PEG, MW=2000), tetraethyl orthosilicate (TEOS), tetrabutyl orthotitanate (TBOT), poly(vinyl pyrrolidone) (PVP, MW=40000) were purchased from Sigma-Aldrich. DMF, HCl, EtOH, MeOH, 2-propanol, acetic acid, aqueous ammonia solution (35%) and acetone were purchased from Fisher. All chemical were used without further purification.

2. Characterization

X-Ray diffraction data were collected on a Bruker D2 phaser in the angular range $2\theta = 5-40^\circ$ employing a Ni $K\beta$ filter (detector side) producing Cu ($K\alpha_1/K\alpha_2$) radiation.

1H -NMR spectra were acquired using a Bruker DPX400 FT-NMR spectrometer. In the case of UiO-66, 5 mg of the dry sample were digested in 700 mL of DMSO and 5 mL of HF (48 % water solution) under sonication.

BET: N_2 adsorption/desorption isotherm was measured at 77 K using a Micromeritics 3-Flex Surface Characterization Analyzer after the sample was first degassed at 120 °C overnight. Surface areas were determined by the BET method in an appropriate pressure range.

Photoluminescence: Steady-state emission spectra were acquired using an Agilent Eclipse Fluorescence Spectrophotometer with a Xenon flash lamp.

TGA: Thermogravimetric analysis (TGA) was performed using a TG 209 F1 Libra (Netzsch) and the sample was heated from room temperature to 900 °C at a rate of 10 °C min^{-1} under an air atmosphere.

UV-crosslinker (CL-1000): Ultraviolet crosslinker equipped with 5 UV-A (365 nm) or UV-C (254 nm) interchangeable lamps (40W).

Xe lamp: an Oriel 150 W Xe lamp equipped with a water-flow IR filter.

3. Synthesis details

Synthesis of UiO-66¹

4 g of ZrCl₄ (17 mmol) was dissolved in a mixture of 400 mL of DMF and 40 mL of HCl under ultrasonication for 20 min. 3.9 g of terephthalic acid (23 mmol) dissolved in 400 mL of DMF was then added and the mixture sonicated for an additional 20 min before heating in oven at 80 °C overnight. After cooling to room temperature, the obtained precipitate was centrifuged (10000 rpm, 12 min) and washed three times with DMF and three times with EtOH. Finally, the white powder was dried at 100 °C for 24 before further characterization.

Synthesis of γ -Fe₂O₃@SiO₂@TiO₂ (FST composites)²

a- Synthesis of Fe₃O₄ microspheres

FeCl₃·6H₂O (1.35 g, 5 mmol) was firstly dissolved in ethylene glycol (40 mL) to form a clear solution, then NaAc (3.6 g) and polyethylene glycol (1.0 g) were added under vigorous stirring. The mixture was transferred to a Teflon lined stainless-steel autoclave (50 mL capacity). The autoclave was heated to and maintained at 200 °C for 8 h, and allowed to cool to room temperature. The black products were washed several times with ethanol and dried at 60 °C overnight.

b- Preparation of Fe₃O₄@SiO₂ (FS) by coating Fe₃O₄ spheres with silica

The SiO₂-coated Fe₃O₄ spheres could be directly processed at room temperature by a modified Stöber method. A typical coating procedure was as follows: 30 mg of Fe₃O₄ spheres were dispersed in a mixed solution of 15 mL of deionized water and 50 mL of 2-propanol. 0.25 mL of TEOS was then added dropwise into the Fe₃O₄ dispersion under mechanical stirring, and the pH value was adjusted to 10 using aqueous ammonia solution. The reaction process was maintained for 2 h at room temperature under continuous stirring. The as-prepared FS spheres were collected with a small magnet and washed three times with 2-propanol and the sample dried at 60 °C overnight.

c- Preparation of γ -Fe₂O₃@SiO₂@TiO₂ (FST) composite microparticles

In a typical synthesis, 0.3 g of FS microspheres were dispersed in a mixed solution of ethanol and TBOT (24 mL ethanol, 0.060 mL TBOT), followed by the addition of PVP (0.01 g). The mixture was then transferred into a 50 mL Teflon container, which was placed into a 200 mL stainless steel autoclave with a Teflon liner. The free space between the two liner walls was filled with 1 mL of distilled water. At the beginning, distilled water did not contact with TBOT. After sealing, the autoclave was heated to 150 °C for 12 h. During the reaction, distilled water vaporized and contacted with TBOT, resulting in TBOT hydrolysis. After the autoclave was cooled to room

temperature, the supernatant was decanted and the resulting precipitate was repeatedly washed with distilled water and ethanol for three times, and then dried at 60 °C in a vacuum oven overnight.

Post-synthetic modification by using TiO₂ and UV-A light

Terephthalic acid: 50 mg of terephthalic acid was dissolved in 100 mL of distilled H₂O and 150 µL of NaOH (1M) added. Then, 250 mg of TiO₂ were added and the mixture was irradiated in the UV-crosslinker equipped with 5 UV-A lamps (40W). After irradiation, 1g of KCl was added to precipitate the TiO₂ and the mixture was kept in the fridge for 6 h. The supernatants were separated with a pipette and the solvent was evaporated.

UiO-66: 200 mg of UiO-66 was dispersed in 300 mL of distilled H₂O and 1 g of TiO₂ was added. The sample was irradiated in the UV-crosslinker equipped with 5 UV-A lamps (40W). The resulting MOF/TiO₂ mixture was dried at 100 °C overnight before further characterization.

It is important to mention that by increasing the pH of the reaction with NaOH, the conversion of the organic linker into bdc-OH was higher. However, due to the low stability of the material at basic pH, the disruption of the framework was greater as observed by PXRD of the resulting MOF.

Post-synthetic modification by using FST composites and UV-A light

Terephthalic acid: 50 mg of terephthalic acid were dissolved in 100 mL of distilled H₂O and 150 µL of NaOH (1M) added. Then, 250 mg of FST composite were added and the mixture was irradiated in the UV-crosslinker equipped with 5 UV-A lamps (40W). After irradiation, FST was separated using a magnet and the water was evaporated.

UiO-66: 50 mg of UiO-66 was dispersed in 100 mL of distilled H₂O and 250 mg of FST composite were added. The sample was irradiated in the UV-crosslinker equipped with 5 UV-A lamps (40W). After irradiation, FST was separated using a magnet and the framework isolated by centrifugation and washed with H₂O and ethanol several times. Finally, the MOF was dried at 100 °C overnight before further characterization.

Post-synthetic modification by using H₂O₂ and UV-C light

50 mg of UiO-66 was dispersed in 100 mL of distilled H₂O and H₂O₂ was added. The sample was irradiated in the UV-crosslinker equipped with 5 UV-C lamps (40W).

After irradiation, the framework was washed with water and EtOH and dried at 100 °C overnight before further characterization.

Interestingly, the same procedure by using terephthalic acid did not give rise to high conversion into bdc-OH, presumably because bdc was not soluble in the reaction conditions. In the case of MOF, H₂O₂ could penetrate into the porous facilitating the hydroxylation.

4. Results

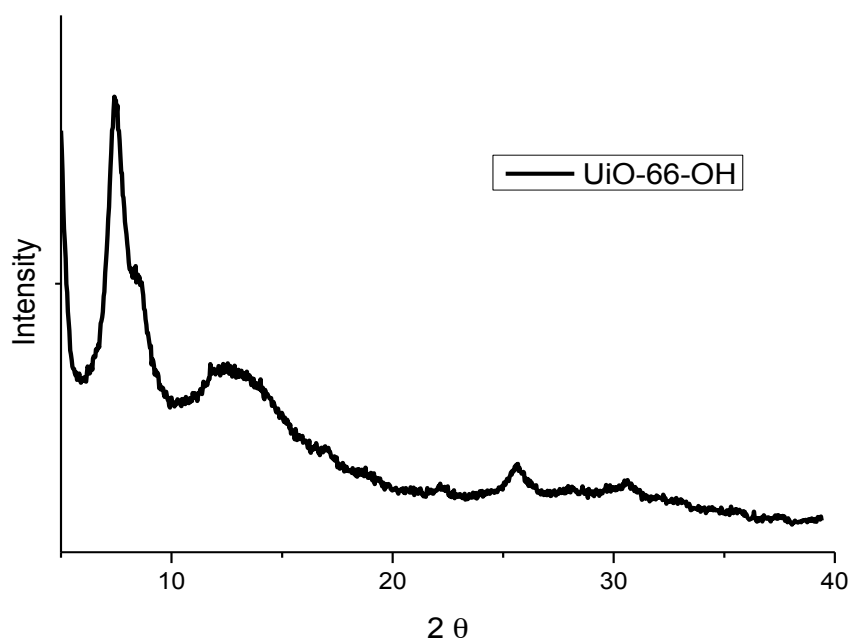


Figure S1. PXRD pattern of UiO-66-OH obtained by using concentrated HCl and DMF as solvents as reported by Farha *et al.*¹

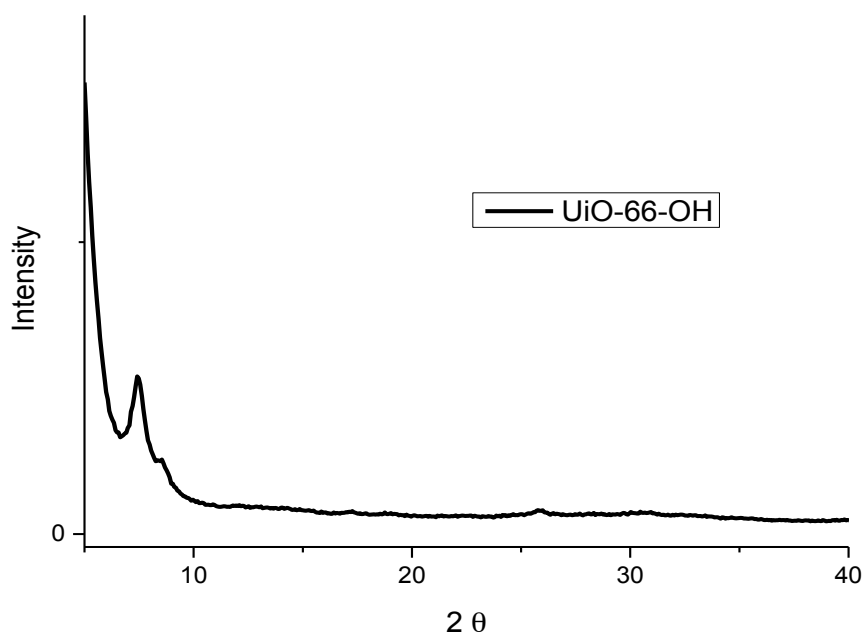


Figure S2. PXRD pattern of UiO-66-OH obtained by using DEF as solvent, as reported by Cohen *et al.*³

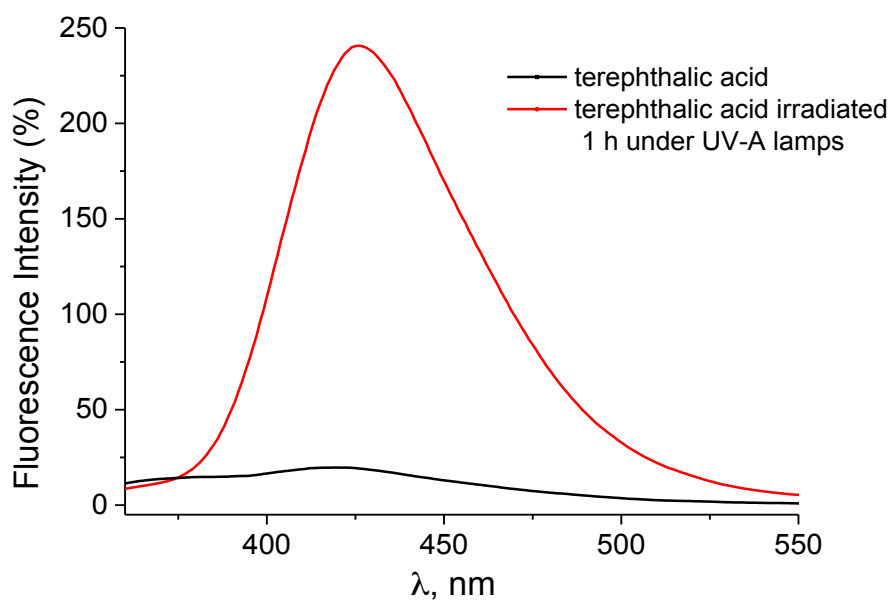


Figure S3. Fluorescence emission of 1.5 mM basic solution of terephthalic acid (bdc) before (black) and after 30 min (red) UV-A irradiation ($\lambda_{\text{ex}} = 315$ nm) in the presence of TiO_2 .

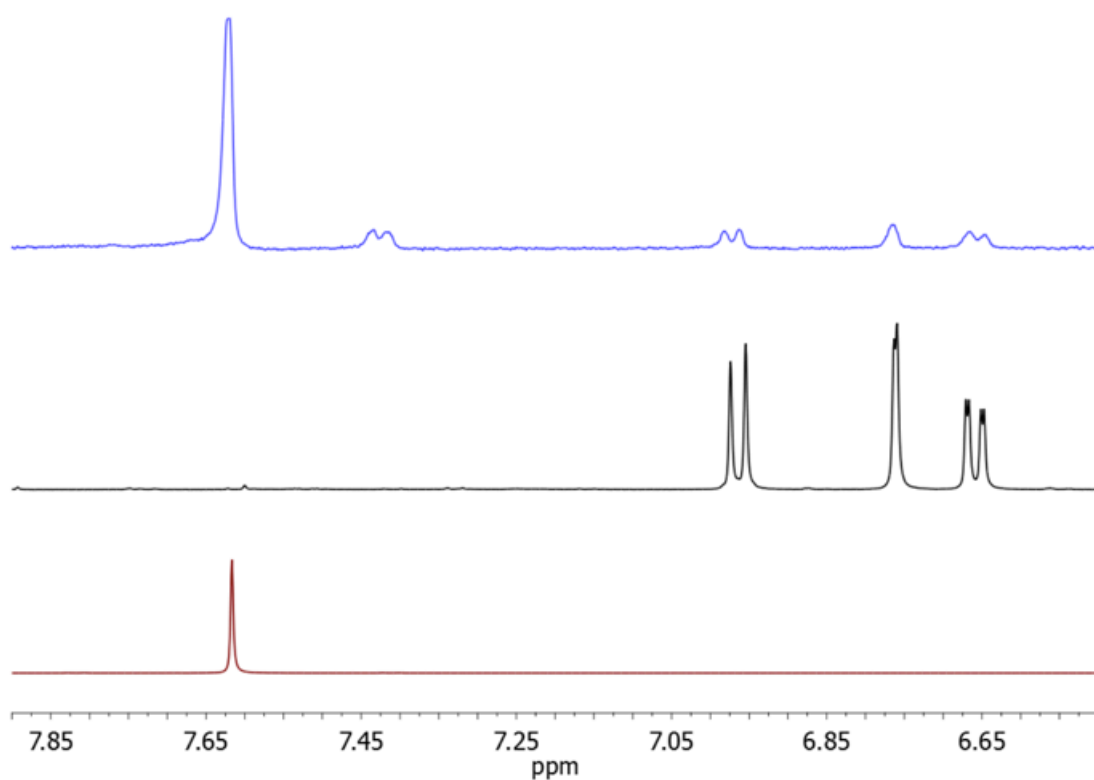


Figure S4. $^1\text{H-NMR}$ spectrum ($\text{D}_2\text{O}/\text{NaOD}$) of UiO-66-OH-47% (blue) achieved by using commercial TiO_2 without further separation. For comparison, bdc (red) and bdc-OH (black) are also shown.

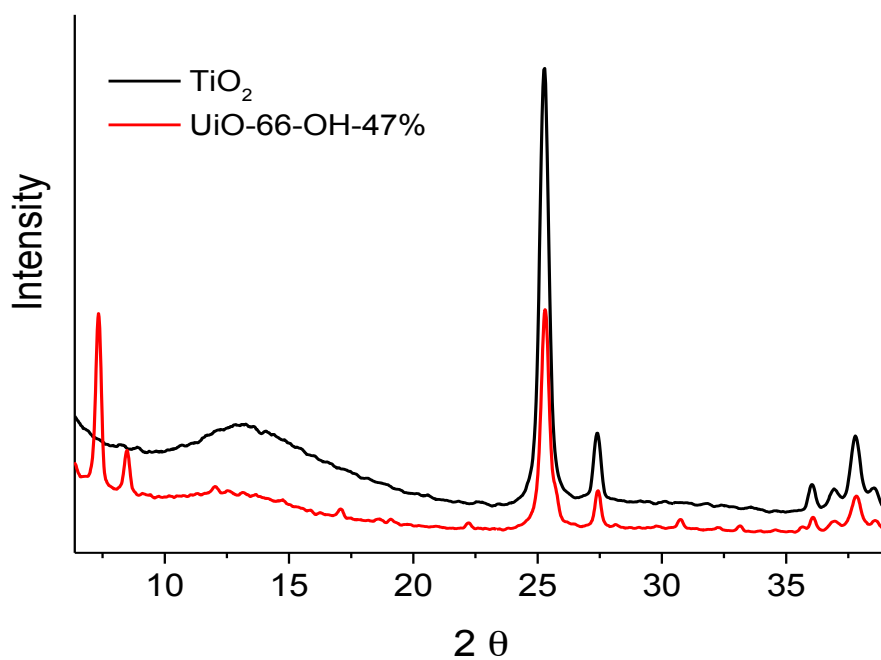


Figure S5. PXRD pattern of UiO-66-OH-47% (red) achieved by using commercial TiO₂ without further separation. For comparison, commercial TiO₂ (black) is also shown. The high amounts of TiO₂ used in the photoreaction make difficult to observe the crystallinity of the resulting UiO-66-OH, and present a challenge to separation.

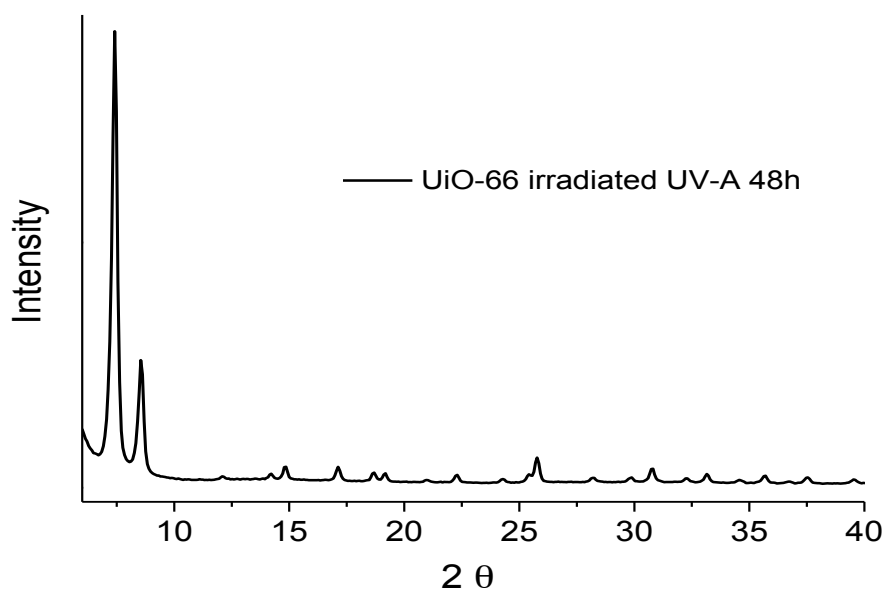


Figure S6. PXRD pattern of UiO-66 after irradiation for 48 h under UV-A lamps in the absence of the TiO₂ photocatalyst indicating high photostability.

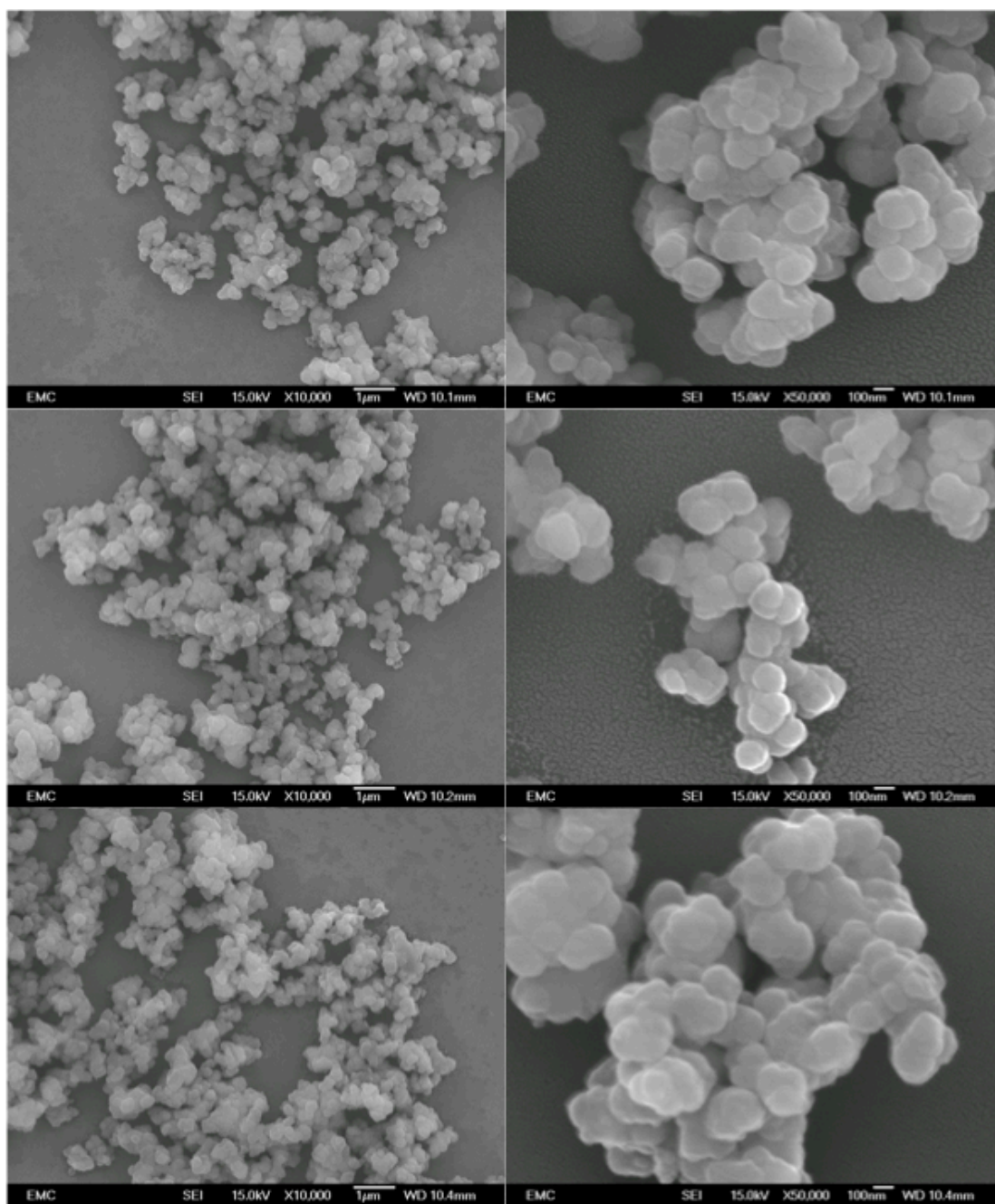


Figure S7. SEM images of UiO-66 (top), UiO-66-OH-49% (middle), and UiO-66-OH-77% (bottom) obtained by using FST and UV-A.

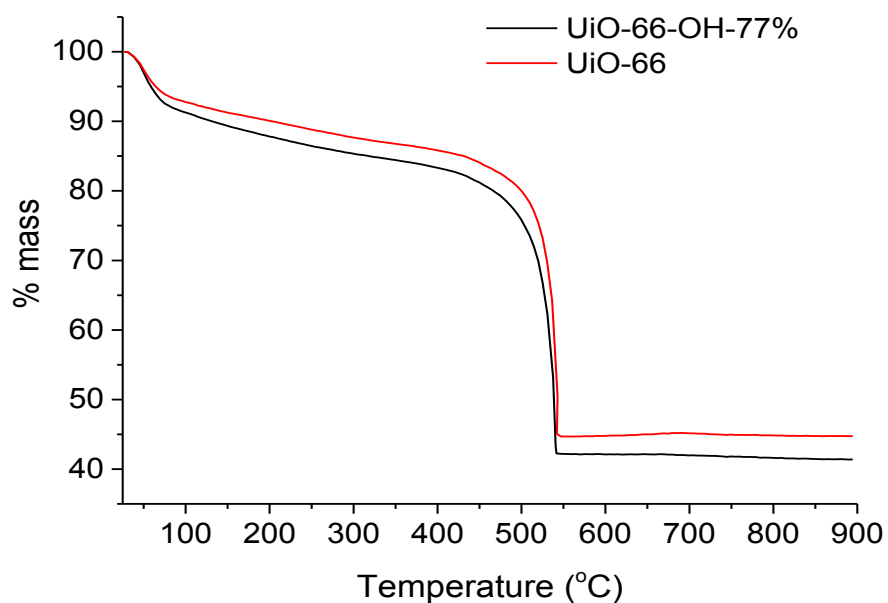


Figure S8. TGA profiles of UiO-66 (red) and UiO-66-OH-77% (black) achieved by using FST composite as photocatalyst under UV-A irradiation.

	Experimental % Mass Loss	Theoretical % Mass Loss
UiO-66	44.7	44.4
UiO-66-OH-77%	42.3	42.6

Table S1. TGA analysis of UiO-66 and UiO-OH-77% (using the molecular formula of $Zr_6O_4(OH)_4(bdc-OH)_{4.6}(bdc)_{1.4}$ for UiO-66-OH-77%).

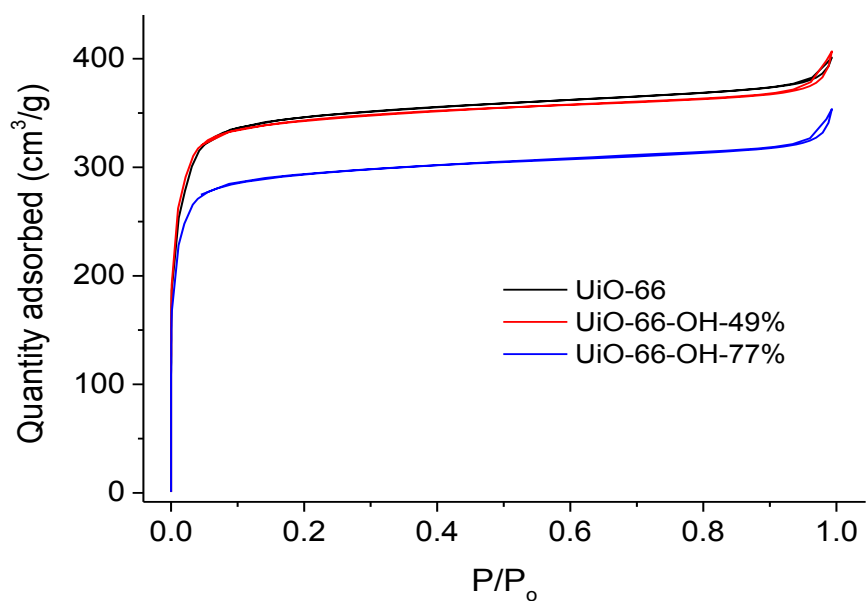


Figure S9. N₂ adsorption isotherms (77 K) of as-synthesised UiO-66, UiO-66-OH-49% and UiO-66-OH-77% achieved by using FST as a photocatalyst under UV-A irradiation.

	BET (m ² /g)
UiO-66	1349 ± 7
UiO-66-OH-49%	1070 ± 33
UiO-66-OH-77%	917 ± 28

Table S2. BET surface areas for UiO-66, UiO-66-OH-49% and UiO-OH-77%.

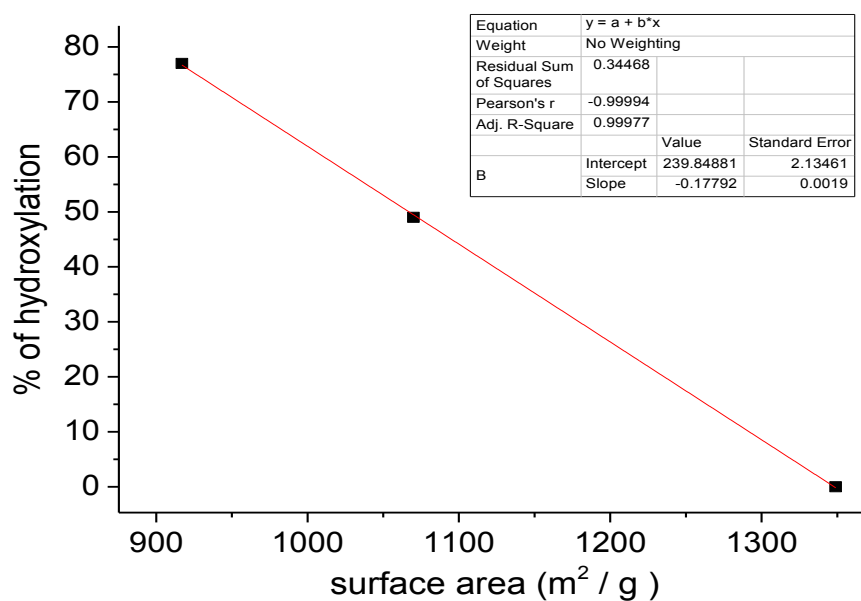


Figure S10. Linear correlation between the degree of hydroxylation (calculated by $^1\text{H-NMR}$) and the BET surface area.

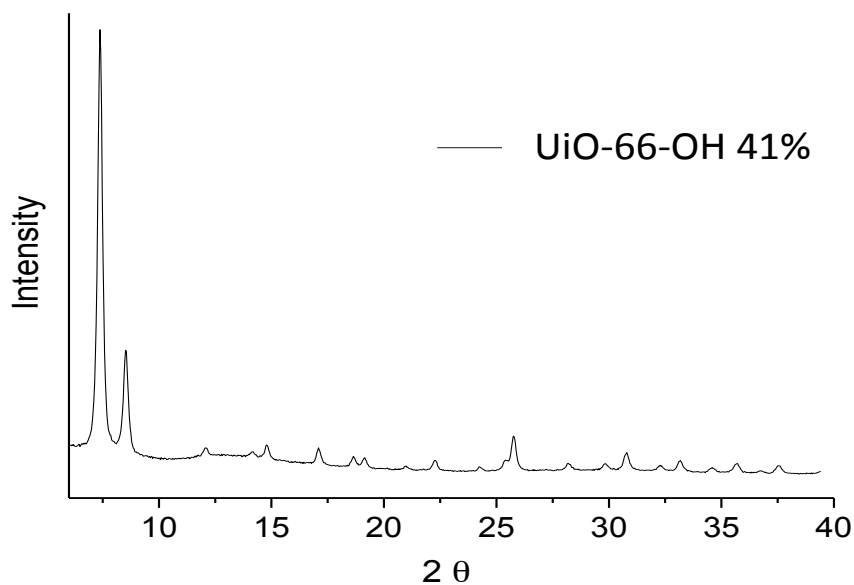


Figure S11. PXRD pattern of UiO-66-OH-41% achieved by using H_2O_2 (10 eq.) in water and UV-C light (40W) for 6h.

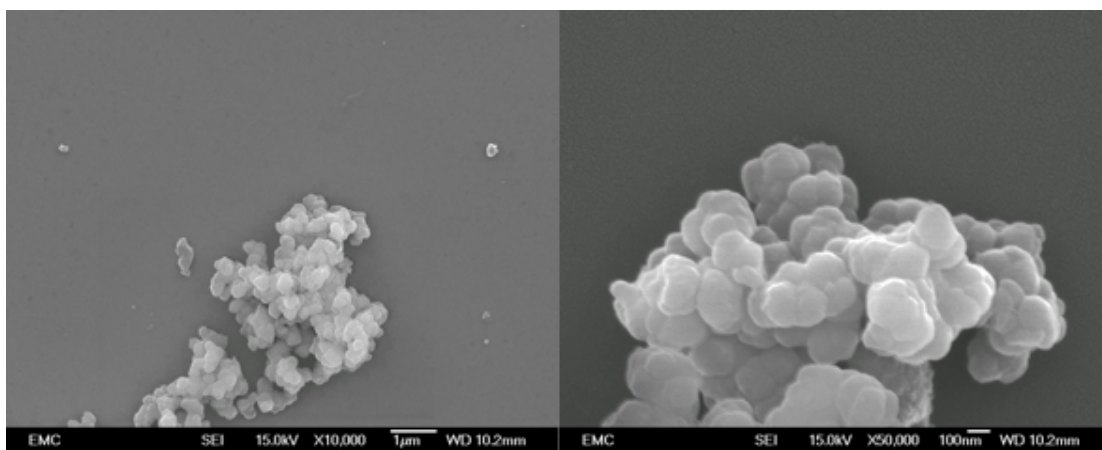


Figure S12. SEM images of UiO-66-OH-41% obtained by using H₂O₂ and UV-C.

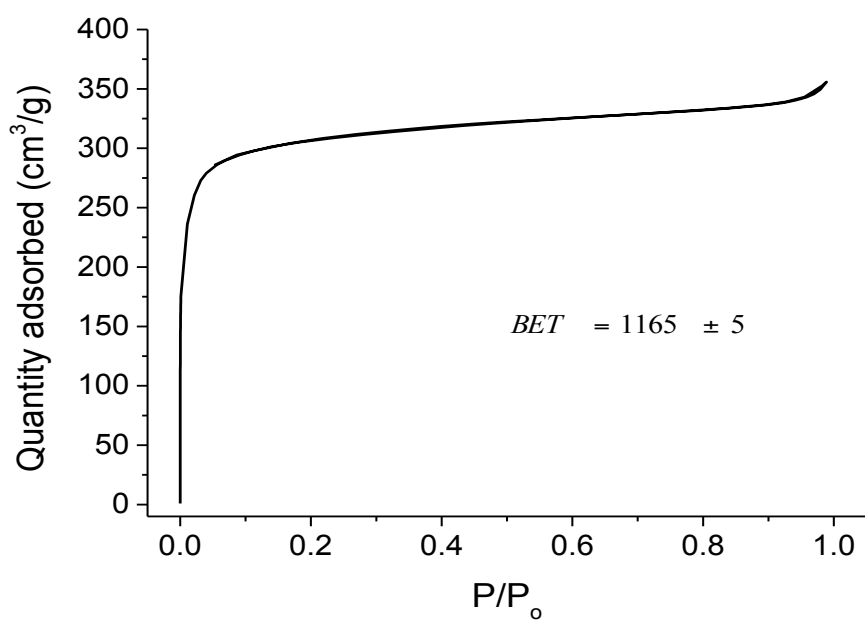


Figure S13. N₂ adsorption isotherm (77 K) of UiO-66-OH-41% achieved by using H₂O₂ (10 eq.) and UV-C light (40W) for 6h.

	24 h	5 days
DMF	11 %	-
THF	9 %	-
H ₂ O	41 %	45 % 53 % ^a

Table S3. Conversions obtained for UiO-66-OH by using PSLE methods. The reactions were carried out at room temperature by following the procedure described by Cohen *et al.* ^a Refers to ratio 10:1 (bdc-OH : UiO-66)

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- 2 X. Yu, S. Liu and J. Yu, *Applied Catalysis B: Environmental*, 2011, **104**, 12.
- 3 M. Kim, J. F. Cahill, Y. Su, K. A. Prather and S. M. Cohen, *Chemical Science*, 2012, **3**, 126.