

# Supporting Information

## **A Generic and Facile Strategy to Metal-Organic Framework Films on TiO<sub>2</sub> Substrates for Photocatalysis**

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## General methods

Starting materials and solvents were purchased and used without further purification from commercial suppliers (Sigma-Aldrich, TCI, Aladdin and others). Proton nuclear magnetic resonance spectra ( $^1\text{H}$  NMR) were recorded on a Advance III (400 MHz). Chemical shifts were quoted in parts per million (ppm) referenced to the appropriate solvent peak or 0 ppm for TMS.

## Experimental procedures

*Preparation of SAM-coated  $\text{TiO}_2/\text{FTO}$  substrate.* FTO was washed with soap water, isopropanol, acetone and water, respectively for 15 min under sonication. A very thin film of  $\text{TiO}_2$  was coated on a FTO glass by spin-coating of 0.15 M titaniumdiisopropoxide bis(acetylacetonate) in 1-butanol at 2000 rpm for 30 s. The spin coated sample was annealed at 500 °C for 15 min. The  $\text{TiO}_2/\text{FTO}$  was then coated with a self-assembled monolayer (SAM) of biphenyl-3,3',5,5'-tetracarboxylate *via* immersing the substrate in a 20 mL DMF solution containing 33 mg biphenyl-3,3',5,5'-tetracarboxylic acid for 24 h, with  $\text{TiO}_2/\text{FTO}$  facing upward.

*Fabrication of UiO-67/ $\text{TiO}_2/\text{FTO}$  film.*  $\text{ZrCl}_4$  (10 mg, 0.04 mmol) and glacial acetic acid (82  $\mu\text{L}$ , 1.4 mmol) was dissolved in 1.5 mL DMF. Then, 4,4'-Biphenyl-dicarboxylic acid (bpdc; 10 mg, 0.04 mmol for thick films and 8 mg, 0.032 mmol for thin films) was dissolved in the solution *via* sonication, and the mixture was sealed in a 20mL scintillation vial. The vial was incubated at 100 °C

for 24 h, followed by cooling down to room temperature and washed extensively with methanol before drying.

*Fabrication of UiO-66/TiO<sub>2</sub>/FTO film.* ZrCl<sub>4</sub> (18 mg, 0.077 mmol) and benzoic acid (675 mg, 5.5 mmol) was dissolved in 4mL DMF. Then 1,4-benzenedicarboxylic acid (*bdc*, 13mg, 0.078mmol for thick films and 10 mg, 0.060 mmol for thin films) was dissolved in the solution via sonication, and the mixture was sealed in a 20mL vial. The vial was incubated at 120 °C for 24 h, followed by cooling down to room temperature and washed extensively with methanol before drying.

*Fabrication of IRMOF-1/TiO<sub>2</sub>/FTO film.* Zn(NO<sub>3</sub>)<sub>2</sub> 6H<sub>2</sub>O (360mg, 1.2mmol) was dissolved in 10mL DEF. Then *bdc* (66mg, 0.4mmol) was dissolved in the solution via sonication, and the mixture was sealed in a 20 mL vial. The vial was incubated at 80 °C for 10 h, followed by cooling down to room temperature and washed extensively with methanol before drying.

*Fabrication of MIL-68/TiO<sub>2</sub>/FTO film.* In(NO<sub>3</sub>)<sub>3</sub> 6H<sub>2</sub>O (21.5mg, 0.05mmol) and glacial acetic acid (10.5 μL, 0.18mmol) was dissolved in 5mL DMF. Then *bdc* (10mg, 0.06mmol for thick films and 8 mg, 0.048 mmol for thin films) was dissolved in the solution via sonication, and the mixture was sealed in a 20 mL vial. The vial was incubated at 100 °C for 24 h, followed by cooling down to room temperature and washed extensively with methanol before drying.

*Ru(bpy)<sub>2</sub>(bpydc) ligand synthesis.* [Ru(bpy)<sub>2</sub>]Cl<sub>2</sub> (160 mg, 0.33 mmol) and 2,2'-bipyridine-5,5'-dicarboxylic acid (*bpydc*, 101 mg, 0.42mmol) were mixed in a solution of EtOH/H<sub>2</sub>O (20mL) and refluxed for more than 20 h under a N<sub>2</sub> atmosphere. After cooling to room temperature, the mixture was filtrated. The filtrate was removed and the solid was recrystallized from a mixture of MeOH and diethyl ether.

*Fabrication of UiO-67-Ru(bpy)<sub>3</sub>/TiO<sub>2</sub>/FTO Film.* Ru(bpy)<sub>2</sub>(bpydc) (37.7mg) was dissolved in 4% KOH solution, and then titrated to pH=7 with 1M HCl. A single piece of air-dried UiO-67/TiO<sub>2</sub>/FTO film was placed at the bottom of the vial with MOF film side facing upwards. The mixture was allowed to react at 75 °C for 24 h. After 24 h, the film was washed with copious amount of MeOH (3 x 10 mL), then incubate in MeOH for further uses.

*Photocatalysis.* UiO-67-Ru(bpy)<sub>3</sub> film (containing 2 mg Uio-67-Ru(bpy)<sub>3</sub>, corresponding to 0.25 mol % Ru) was suspended in a 10 mL methanol solution containing 100 μL thioanisole (0.82 mmol). The reaction was stirred at the room temperature in air at a distance of 10 cm from a 3 nm blue LED (440 nm) for 24 h. After each recycle, the film was immersed in methanol for several hours to remove the product for next recycle. The resultant mixture was analyzed by <sup>1</sup>H NMR. For powdered sample, 2 mg powder was added into a 10 mL methanol solution containing 100 μL thioanisole (0.82 mmol). After the 24 h reaction, the catalyst and the reaction solution was separated *via* centrifugation, and the catalyst was immersed in methanol for several hours before the next catalytic run.

*Stability test.* MOF films were suspended in a 10 mL methanol solution for 24 h. After then, MOF films were dried in air, followed by PXRD and SEM characterization.

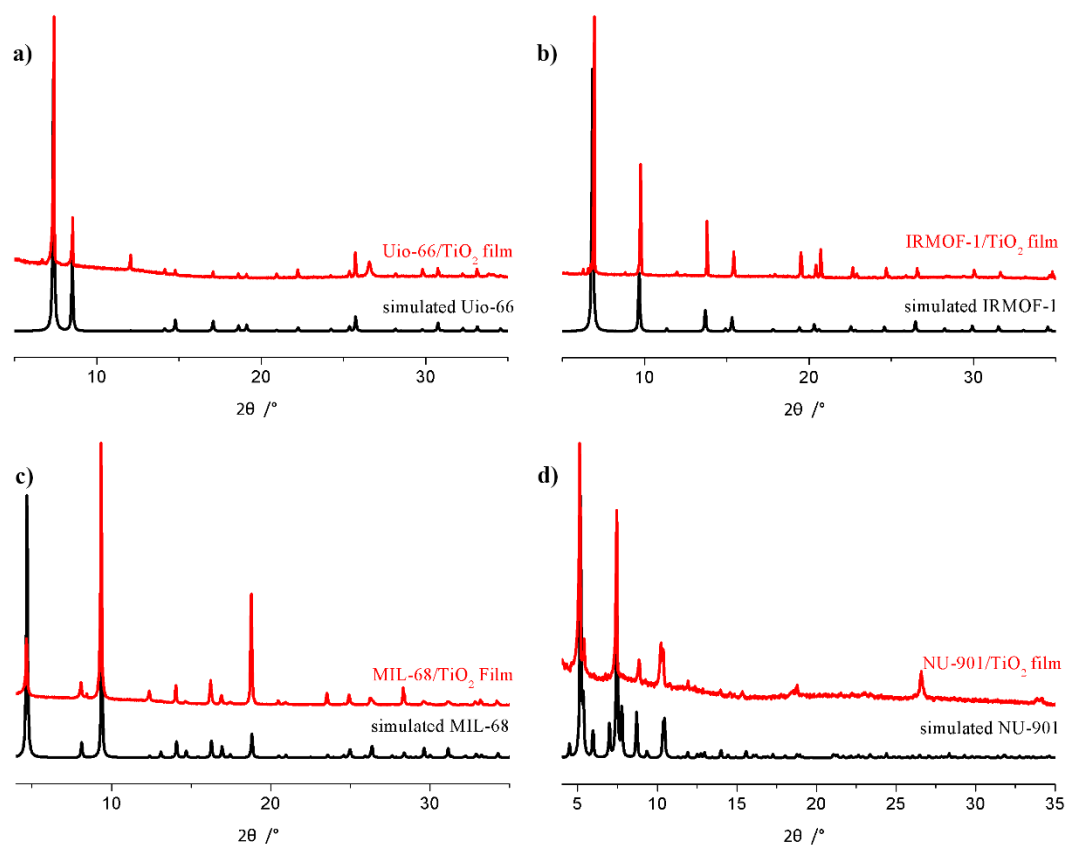
*Adhesive tape peel test.* MOF films were dried in air, an adhesion tape (3M 600#) was used to peel the films from the FTO substrate. The pressing and peeling process was carried out three times for each film.

*Powder X-ray Diffraction (PXRD) Analysis.* MOF films were air-dried prior to PXRD analysis. PXRD data were collected at ambient temperature on a Bruker D8 Advance diffractometer at 40 kV, 40 mA for Cu K $\alpha$  ( $\lambda= 1.5418 \text{ \AA}$ ), with a scan speed of 1 sec/step, a step size of  $0.02^\circ$  in  $2\theta$ , and a  $2\theta$  range of  $\sim 5$  to  $35^\circ$  (sample dependent).

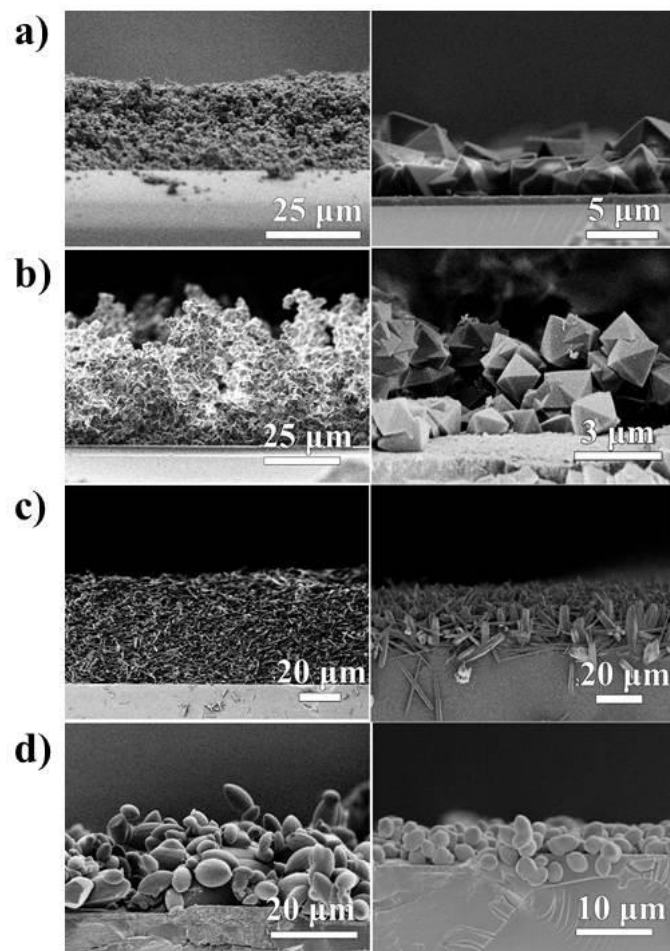
*Scanning Electron Microscopy (SEM).* MOF films were transferred to conductive carbon tape on a sample holder disk, and coated using an Au-sputter coating. A Hitachi S4800 was used for acquiring images using a 1-3 kV (sample dependent) energy source under vacuum.

*Inductive Coupled Plasma Emission Spectrometry (ICP).*  $\sim 5\text{mg}$  UiO-67-Ru(bpy) $_3$  was scraped from MOF/TiO $_2$  film and dissolved in a diluted HNO $_3$  solution via sonication. ICP data was collected on a PE 8300 Inductive Coupled Plasma Emission Spectrometer.

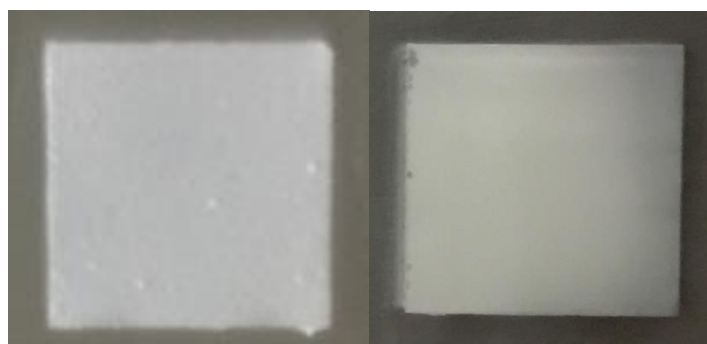
## Supporting Figures and Tables



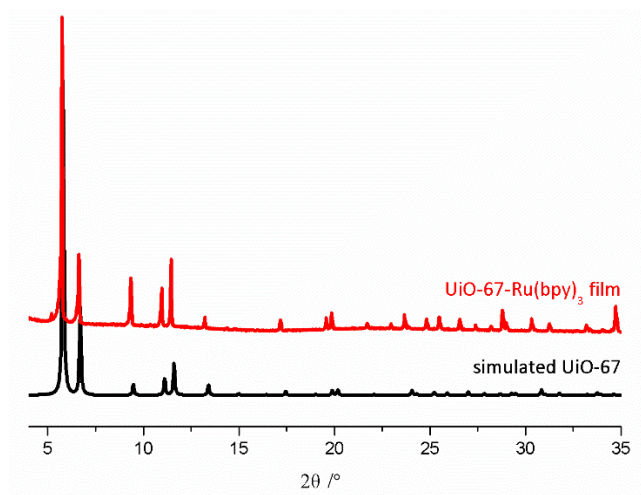
**Figure S1.** Experimental and simulated PXRD of UiO-66(a), IRMOF-1(b), MIL-68(c), and NU-901(d) films.



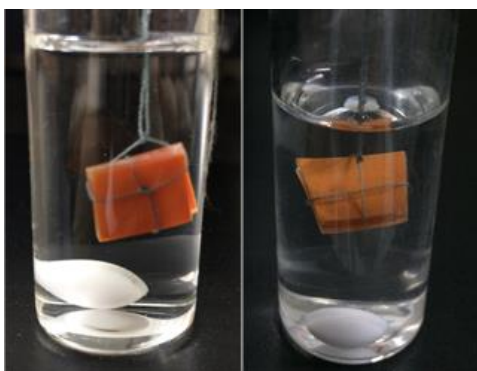
**Figure S2.** Cross-sectional FE-SEM images of UiO-67(a), UiO-66(b), MIL-68(c), and NU-901(d) films as thicker one (left) and thinner one (right).



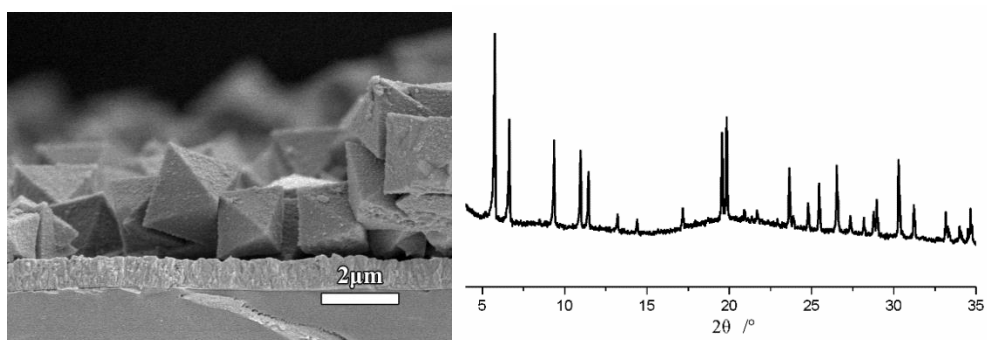
**Figure S3.** Photographs of UiO-67 film before (left) and after (right) adhesion tape peel test.



**Figure S4.** Experimental and simulated PXRD of UiO-67-Ru(bpy)<sub>3</sub>/TiO<sub>2</sub>/FTO film.

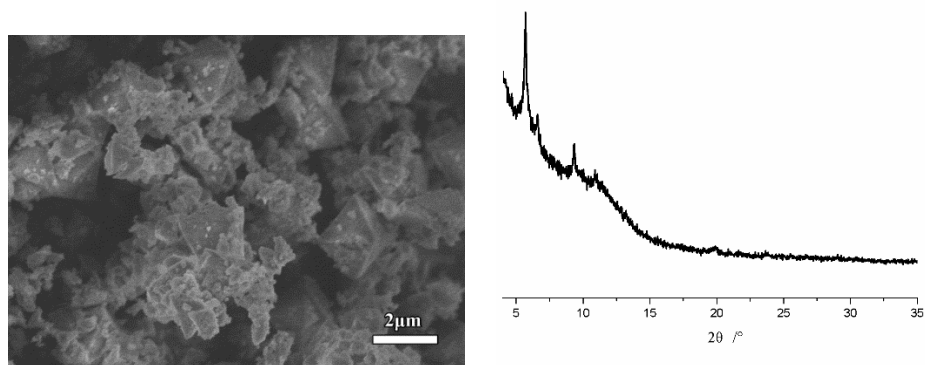


**Figure S5.** UiO-67-Ru(bpy)<sub>3</sub> films before (left) and after (right) 8 catalytic cycles.

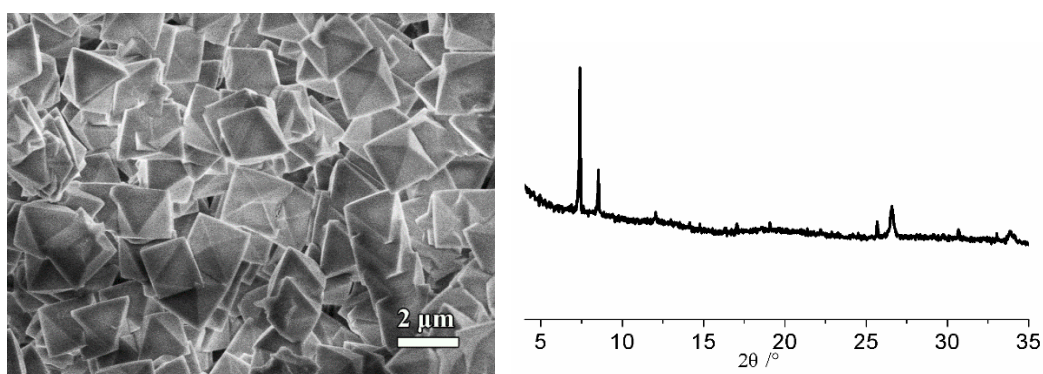


**Figure S6.** FE-SEM (left) and PXRD (right) of UiO-67-Ru(bpy)<sub>3</sub>/TiO<sub>2</sub>/FTO film after 8 catalytic cycles.

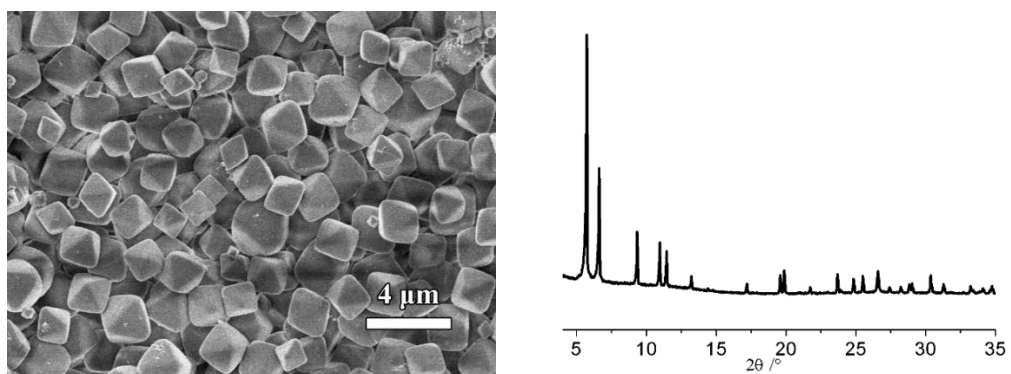




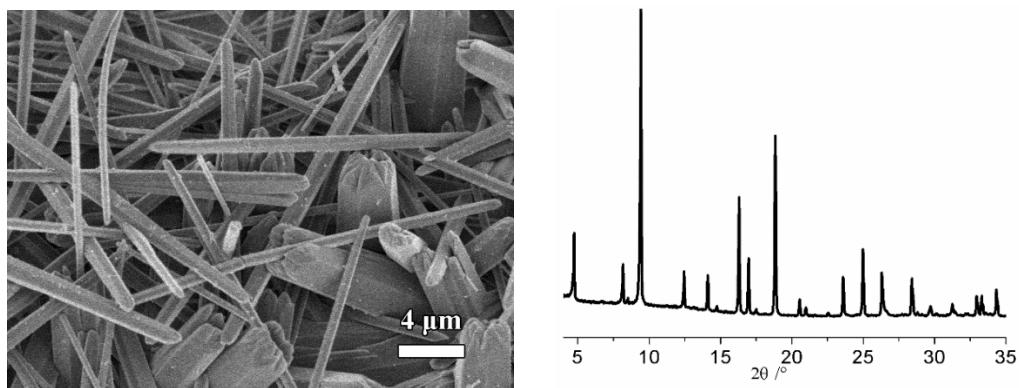
**Figure S7.** FE-SEM (left) and PXRD (right) of UiO-67-Ru(bpy)<sub>3</sub> powder after 5 catalytic cycles.



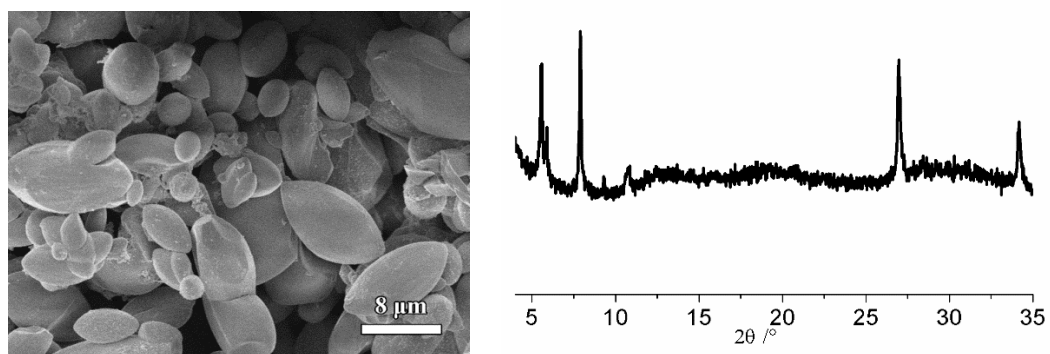
**Figure S8.** FE-SEM (left) and PXRD (right) of UiO-66 films after incubation in methanol for 24 h.



**Figure S9.** FE-SEM (left) and PXRD (right) of thicker UiO-67 film after incubation in methanol for 24 h.



**Figure S10.** FE-SEM (left) and PXRD (right) of MIL-68 film after incubation in methanol for 24 h.



**Figure S11.** FE-SEM (left) and PXRD (right) of NU-901 film after incubation in methanol for 24 h.