Supporting Information Material

Bi_2O_3 nanoparticles encapsulated in surface mounted metal-organic frameworks thin films

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Materials and Methods:

X-ray Diffraction (XRD): Each sample was characterized by using a Bruker D8 Advance equipped with a Si-strip detector (PSD Lynxeye©; position sensitive detector) with Cu $K_{\alpha1,2}$ radiation (λ = 0.15418 nm) in θ–θ geometry, variable slit on primary circle. Scans were run over various ranges with step width of 0.024° 2θ and 84 seconds, for higher order peaks up to 336 seconds per step. The 2θ angle scanning range to observe corresponding peak to deposited film is picked 5° to 60°.

Infrared reflection absorption (IRRA) spectroscopy: IRRA spectra were measured using the infrared spectrometer (Bruker VERTEX 80) purged with dried air. The spectra were recorded in grazing incidence reflection mode at a fixed angle of incidence of 80° relative to the surface normal using mercury cadmium telluride (MCT) detector. Perdeuterated hexadecanethiol SAM on Au/Ti/Silicon substrates were used for reference measurements.

Scanning electron microscopy (SEM): HR-SEM cross-sectional measurements have been performed on a Zeiss HR-SEM (Gemini Class) at 3-5 kV to check the continuity, compactness, and homogeneity of the different prepared (loaded and unloaded) HKUST-1 thin films.

Quartz Crystal Microbalance (QCM): A quartz crystal microbalance (QCM) was employed to growth an HKUST-1 SURMOF thin film on a QCM sensor in a clean and well-controlled manner to further perform the uptake $BiPh_3$ experiments. The QCM sensor was placed in a flow cell (Q-Sense E4). Infiltration with guest

molecules was achieved via a stream of liquid through the cell. The grown SURMOF QCM sensor was grown directly on gold wafer, which was functionalization with a 16-mercaptohexadecanoic acid self-assembled monolayer (MHDA SAM). SURMOF growth was carried out in situ in the QCM flow cell by alternating between the metal source solution (1 mM copper(II) acetate), a solution of 0.2 mM 1,3,5-benzenetricarboxylic acid (BTC) in ethanol and pure ethanol as described previously.

The *UV-Vis spectra* were recorded in the range of 200 nm to 800 nm by means of a Cary5000 spectrometer with a UMA unit from Agilent. The UV-Vis spectra of the SURMOFs on the quartz substrate were measured in transmission mode.

Transmission electron microscopy (TEM): Plane-view measurements have been performed using an image aberration corrected FEI Titan 80-300 operated at 300 kV and equipped with a Gatan US1000 CCD camera for TEM and SAED analysis and a Fischione HAADF detector for STEM imaging. An EDAX S-UTW detector was used for EDX analysis. The SAED and STEM analysis was performed at LN_2 temperatures to reduce electron beam damage of the HKUST-1. For TEM measurement, samples were prepared by remove the Bi_2O_3@HKUST-1 thin films from quartz-glass sample surface through a laser ablation-process (see Fig. S1) and transfer the thin films onto a holey carbon Au grid (Quantifoil GmbH).

Laser-Ablation Process: Bi_2O_3@HKUST-1 has been directly grown on HR-TEM grids or was deposited as crystal-pieces through a laser micromachining process. The latter approach was performed by laser lift-off initiated by selective laser ablation using an excimer laser radiation source operating at a wavelength of 248 nm with a pulse length of 5 ns.[1]

Molecular modeling simulations were performed using a Monte Carlo algorithm implemented in the simulation package SIMONA with Lennard-Jones and Coulomb interaction. For details on geometry optimization (using DFT) and the force field parameters, see reference. The Lennard-Jones parameters of Bi were set to 1.7295 kcal/mol and 2.8 Å.[2]

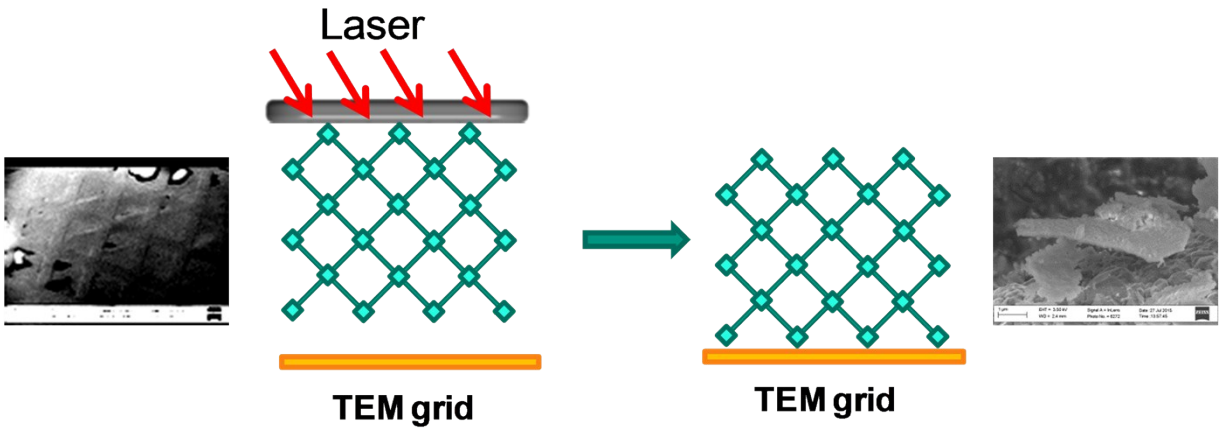
Time-of-flight secondary ion mass spectrometry (ToF-SIMS) was performed on a TOF.SIMS 5 instrument (ION-TOF GmbH, Münster, Germany). For all experiments a short pulse width (2 ns) 20 keV C_{60}^+ ion beam was applied as analysis beam. For quasi-static SIMS this beam was rastered over 500×500 μm^2 and the dose density was limited to below 10^{11} ions/cm^2 (static limit). For dynamic SIMS, an additional O_2^+ beam (500 eV) was applied for erosion of a 450×450 μm^2 field with a concentric analysis field of 250×250 μm^2. Spectra calibration was performed on C, Cu, Bi, and Bi_3O_4 peaks, mass deviations were below 20 ppm.

Electrospray ionisation mass spectrometry (ESI-MS) was

The Bi_2O_3 thin film sample for the XPS measurement was grown on the silicon wafer using the liquid deposition method. The deposition solution was using the $BiPh_3$ solution which after irradiated with 255 nm UV light for 5 h.

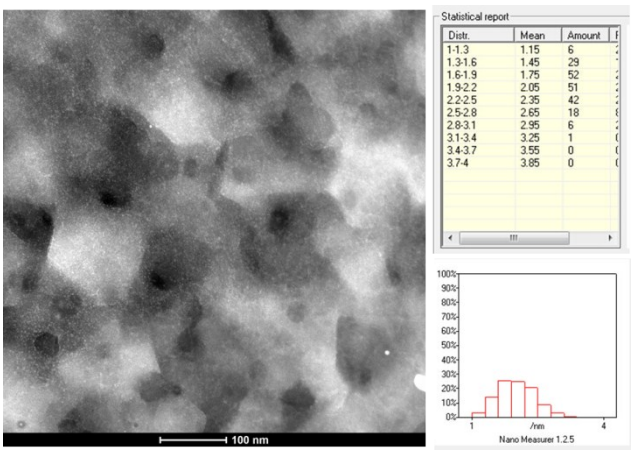
All HKUST-1 SURMOFs used in the present work were grown on modified Au substrates using the liquid-

phase epitaxy (LPE) method,[1] except parts of TEM and UV-vis samples were grown on quartz glass. The surface modification was carried out by depositing a SAM (self-assembled monolayer) made from 16-mercaptohexadecanoic acid (MHDA, 99%, Aldrich). The SURMOFs were fabricated using a spray system, as described in detail in an earlier publication.[3] The spray times were 15 s for the copper acetate solution and 25 s for the BTC solution. Each spray step was followed by a rinsing step (3 s) with pure ethanol to remove residual reactants. A total of 20-35 growth cycles were used for all SURMOFs investigated in this work. Before further processing, all SURMOFs samples were activated by ultrasound in dichloromethane solution for 5 min to remove residual solvent from the SURMOFs pores and characterized by X-ray diffraction (XRD) (see Fig. 2b). Cross-sectional images recorded by scanning electron microscopy (SEM) demonstrate that the thickness of SURMOFs amounts to about 100 nm (see also Fig. S2). For $BiPh_3$ loading, a HKUST-1 SURMOF was placed into a 250 ml flask, which was then evacuated to 200 Pa at room temperature (RT) for 30 min. Subsequently, a freshly prepared solution of $BiPh_3$ (triphenylbismuth) in ethanol (1 mM, Aldrich) was injected quickly into the reaction flask and heated to 65˚C for 36 h. $BiPh_3$ is a simple organo-bismuth compound which is quite stable under normal conditions.[4] The loading of $BiPh_3$ into the HKUST-1 SURMOFs was analyzed in a quantitative fashion using a quartz crystal microbalance (QCM) (see Fig. S3). The mass density of the activated framework amounts to 0.98 $g \cdot cm^{-3}$, which is increased by the ethanol contained in the pores, yielding a total mass-density of the ethanol-soaked HKUST-1 of 1.53 $g \cdot cm^{-3}$.[5] A quantitative analysis of the QCM-data yields a $BiPh_3$ loading of ~ 0.17 g $BiPh_3$ per 1 g ethanol-soaked HKUST-1. This corresponds to a loading of 2-3 $BiPh_3$ molecules per HKUST-1 unit cell. After loading $BiPh_3$, the reaction flask with $BiPh_3$@HKUST-1 sample was taken out from the oven and irradiated with 255 nm UV light for 5 h. Upon irradiation, the solution turns from clear to opaque (Fig. S4). Subsequently, the sample was removed from the reaction solution, rinsed with pure ethanol and dried in dry N_2 gas. Then, the sample was irradiated with 255 nm UV light for 1 h.



(a)

(b)



(c)

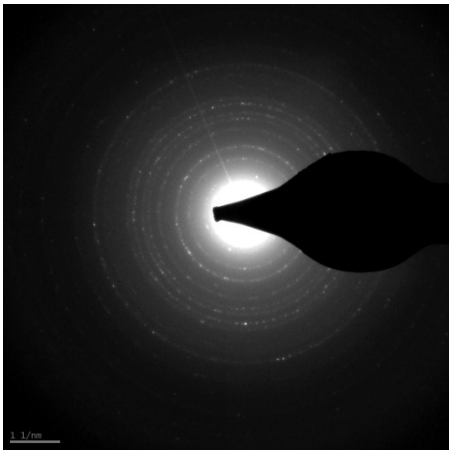


Figure S1. Synthesis scheme of the Bi_2O_3@HKUST-1 SURMOFs TEM sample preparation by a laser ablation process. b) HR-TEM of embedded Bi_2O_3 NPs in the surface of oriented HKUST-1 SURMOF. (c) cryo-SAED diffraction pattern of deposited HKUST-1 thin films, see also TableS1.

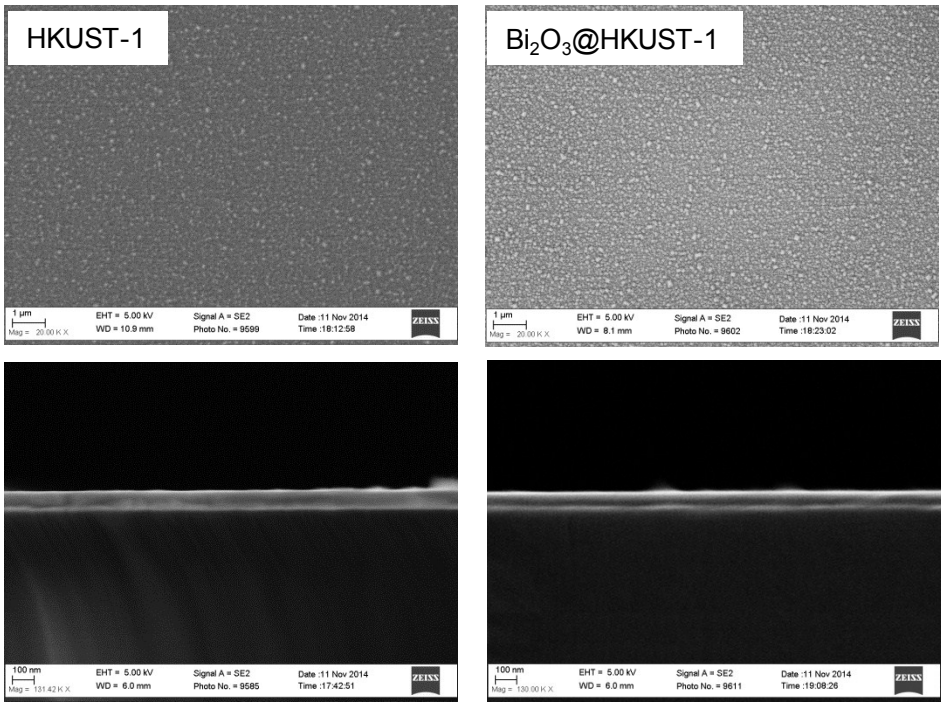
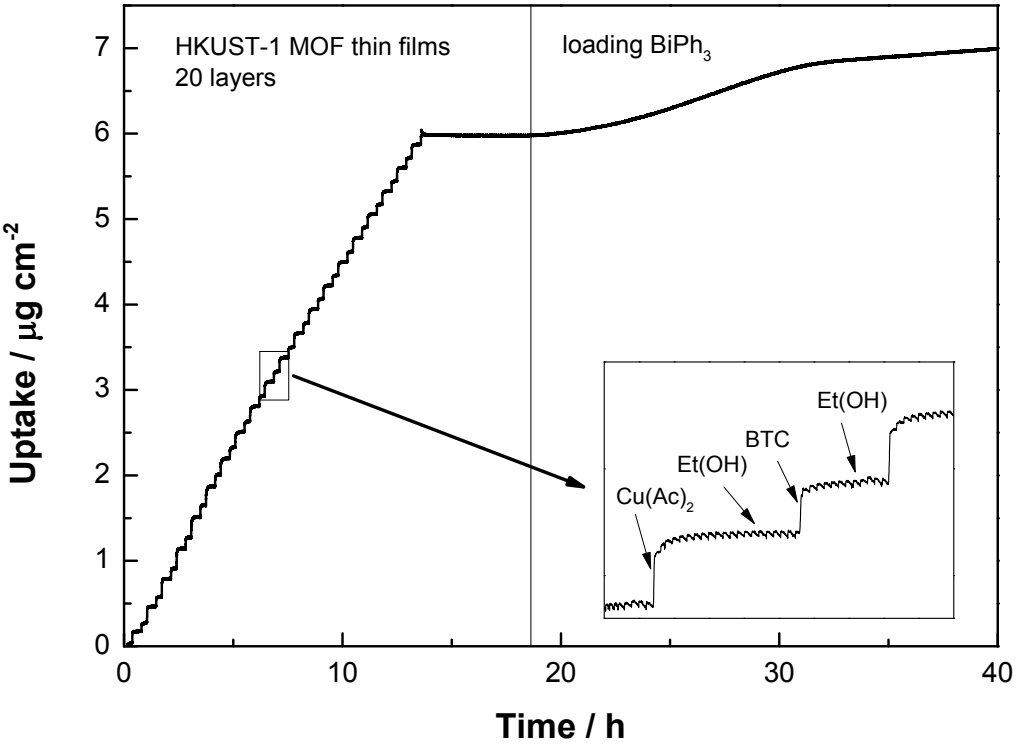


Figure S2. Scanning electron micrograph (SEM) of 20 cycles of $Cu_3(BTC)_2$ MOF thin films (left) and after loading Bi_2O_3 (right).



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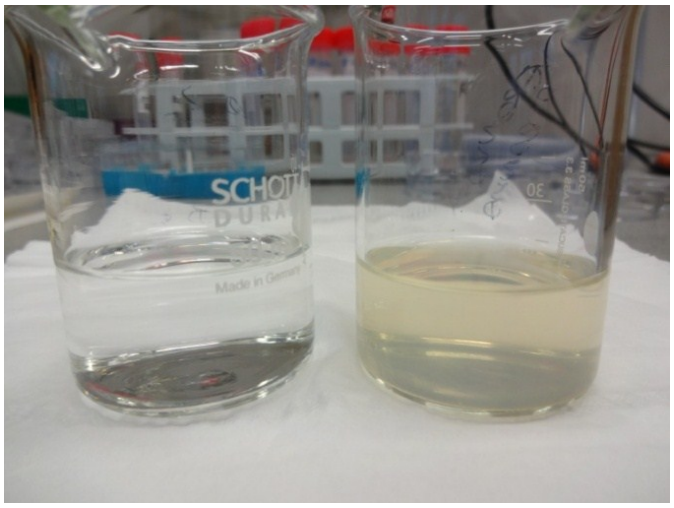
104 Figure S3. Layer-by-layer growth of the HKUST-1 SURMOF on the QCM sensor with 20 cycles and performed
105 uptake experiment with $BiPh_3$. The inset is a magnification of the layer-by-layer growth of the SURMOF. (The
106 small oscillations in the curve is from the pump)



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108 Figure S4. $BiPh_3$ ethanolic solution before irradiation (left) and after irradiation (right).

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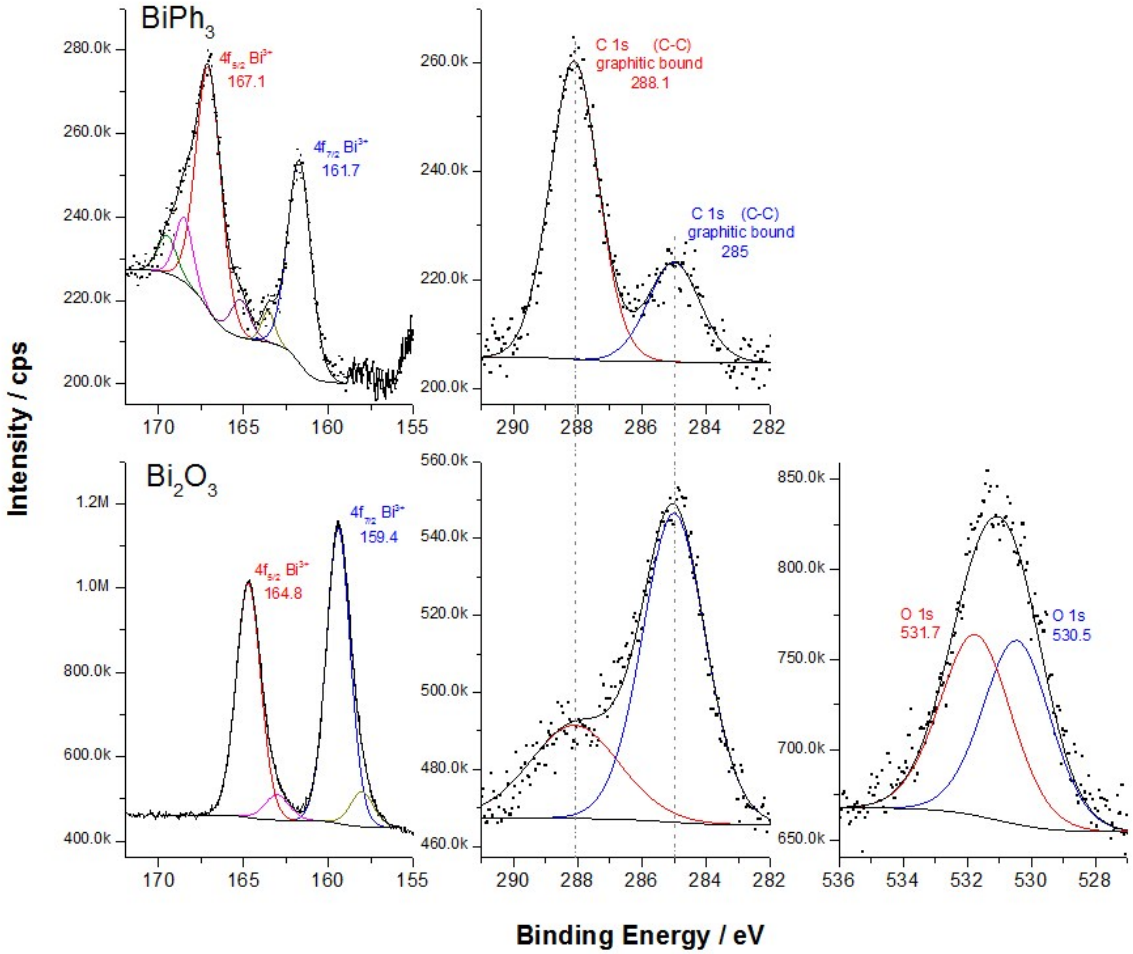


Figure S5. X-ray photoelectron spectrum (XPS) analysis for $BiPh_3$ (up) and Bi_2O_3 (down).

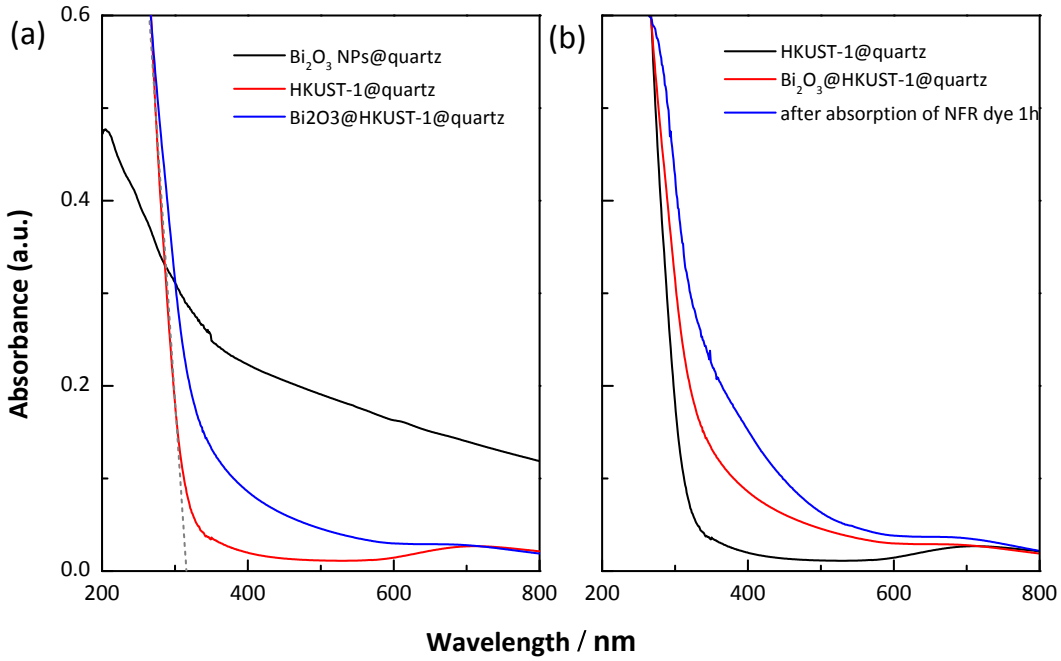
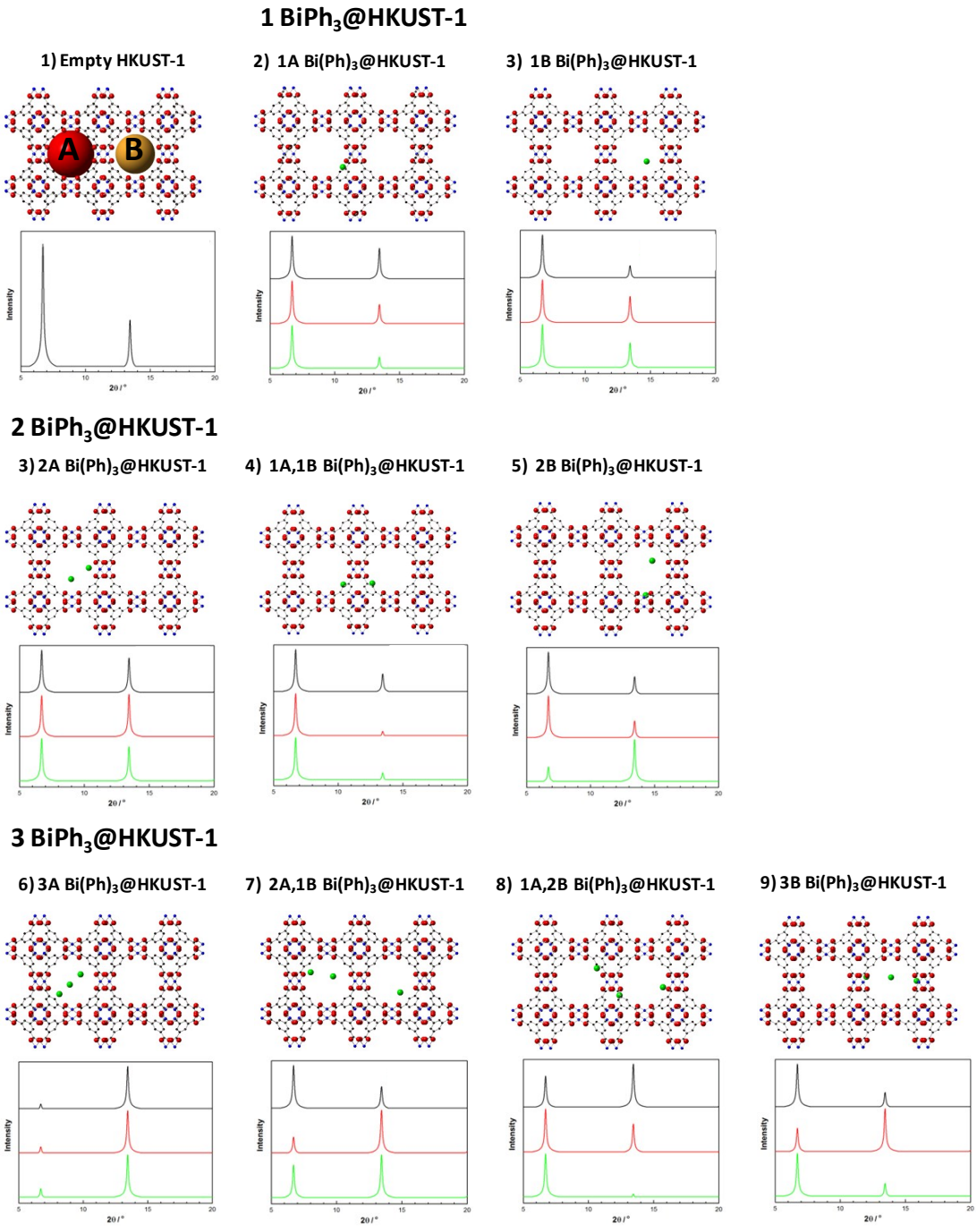


Figure S6. (a) UV-Vis absorption spectra of the Bi_2O_3 thin films on quartz glass (black), HKUST-1 SURMOFs (red) and Bi_2O_3@HKUST-1 SURMOFs (blue). (b) UV-Vis absorption spectra of HKUST-1 SURMOFs (black), Bi_2O_3@HKUST-1

115 SURMOFs (red) and Bi_2O_3@HKUST-1 SURMOFs after absorption of NFR dye 1 h (blue).



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117 Figure S7. Schematic structure of HKUST-1 (1) (large pore: A, middle pore: B) and after loading different number
118 [single Bi^{3+} in A (1), single Bi^{3+} in B (2), 2 Bi^{3+} in A (3), 1 $Bi(Ph)_3$ in A and 1 Bi^{3+} in B (4), 2 Bi^{3+} in B (5), 3 Bi^{3+} in A (6),
119 2 Bi^{3+} in A and 1 Bi^{3+} in B (7), 1 Bi^{3+} in A and 2 Bi^{3+} in B (8), 3 Bi^{3+} in B (9)]. Calculated X-ray diffraction patterns for
120 HKUST-1 before and after loading Bi^{3+} in different plane [(001) plane (up, black line), (010) plane (middle, red line)
121 and (100) plane (down, green line)]. The anion was hidden.

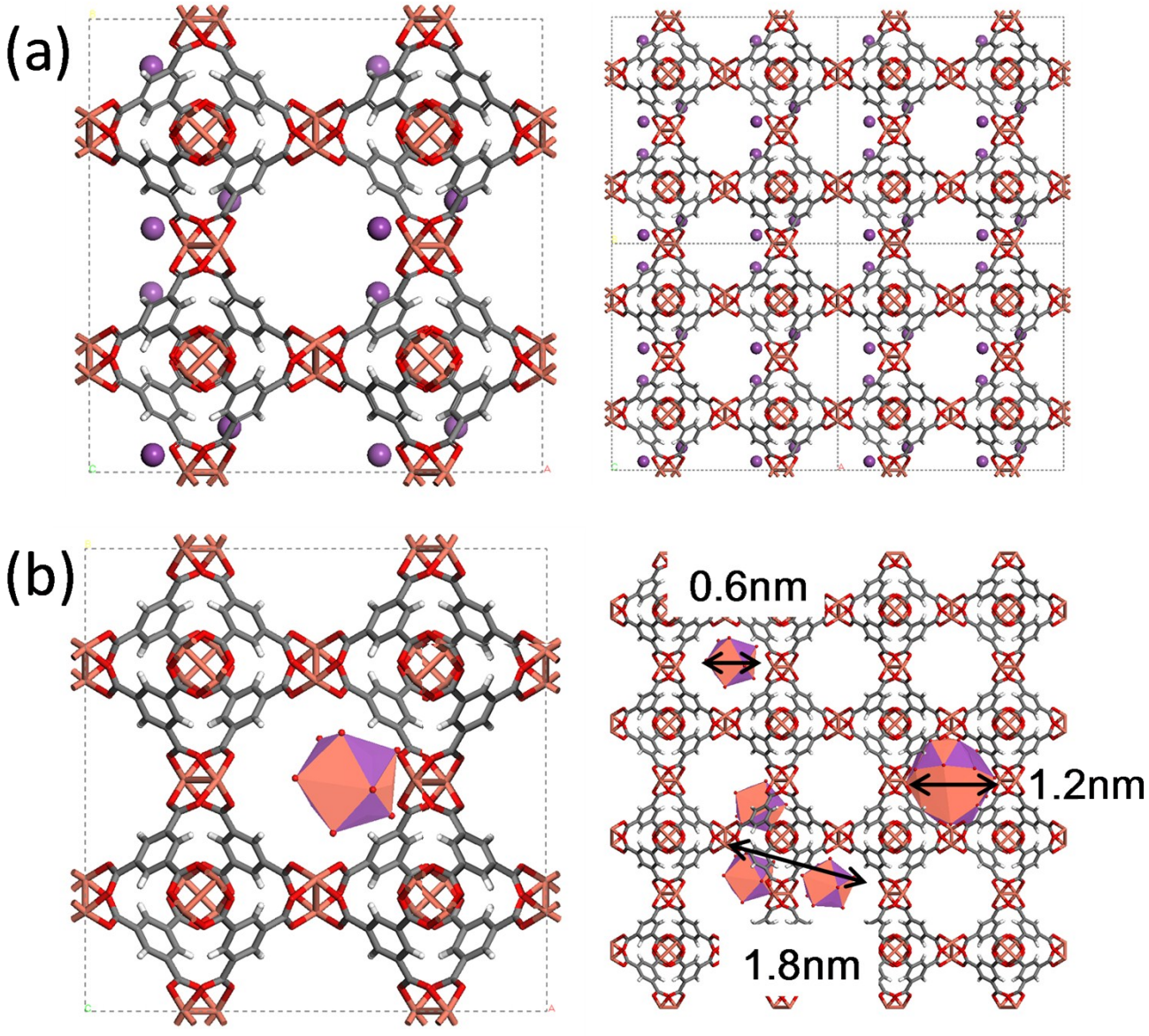
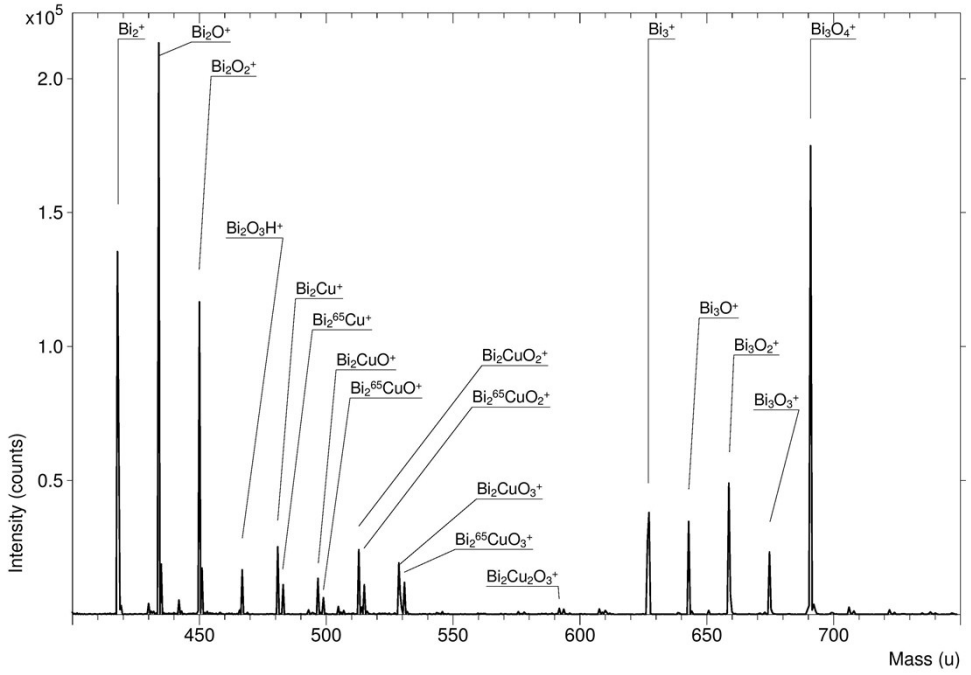


Figure S8. a) Infiltration of three $BiPh_3$ molecules inside an HKUST-1 pore. b) Model of photosynthesized $(Bi_2O_3)_n$ Clusters/NPs with *n* = 1-5 in the defined pore-space of HKUST-1, avoiding sintering with particles from adjacent pores.



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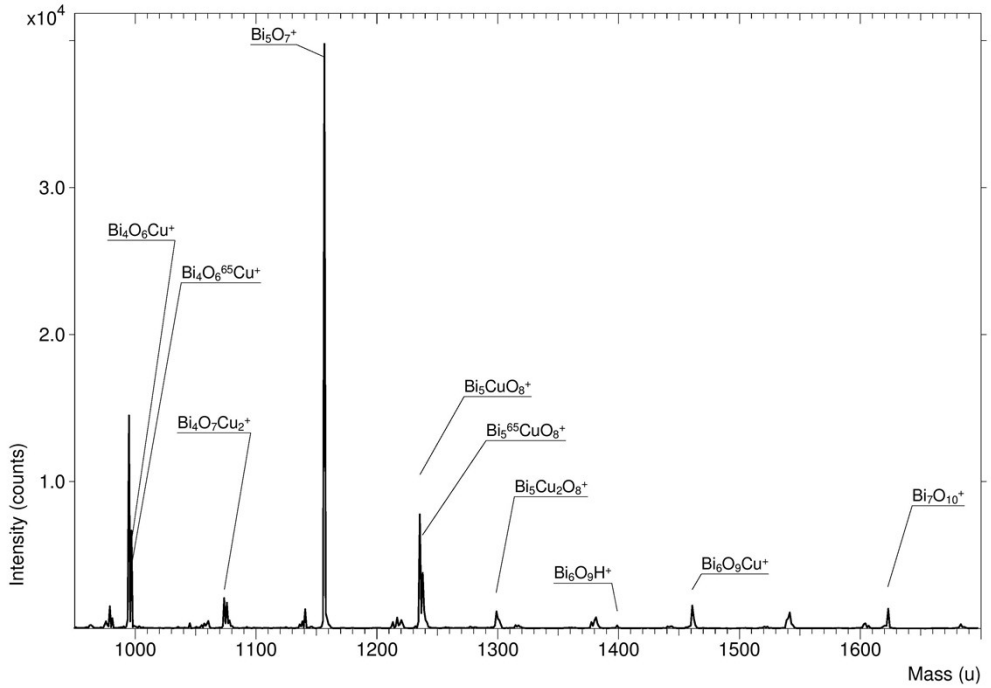
127 Figure S9. Quasi-static SIMS of a Bi_2O_3@HKUST-1 SURMOF stack performed with C_{60} (20 keV) bunched. 400 < m/z
128 < 750.



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130 Figure S10. Quasi-static SIMS of a Bi_2O_3@HKUST-1 SURMOF stack performed with C_{60} (20 keV) bunched. 950 <

m/z < 1700

As shown in Figs. S9 and S10, the positive polarity secondary ion mass spectrum obtained under quasi-static conditions from a Bi_2O_3@HKUST-1 SURMOF stack is dominated by several bismuth oxides and $Bi_xO_yCu_z$ cluster ions. The bismuth oxide fragment Bi_2O shows highest intensity (212 kcts) followed by Bi_3O_4 (170 kcts), Bi_4O_5 17 (kcts), and Bi_5O_7 (39 kcts). A marked drop in intensity is observed for bismuth oxide clusters bigger than Bi_5O_y. Bi_6O_9 is not detectable, Bi_7O_{10} has an intensity of only 1 kcts.

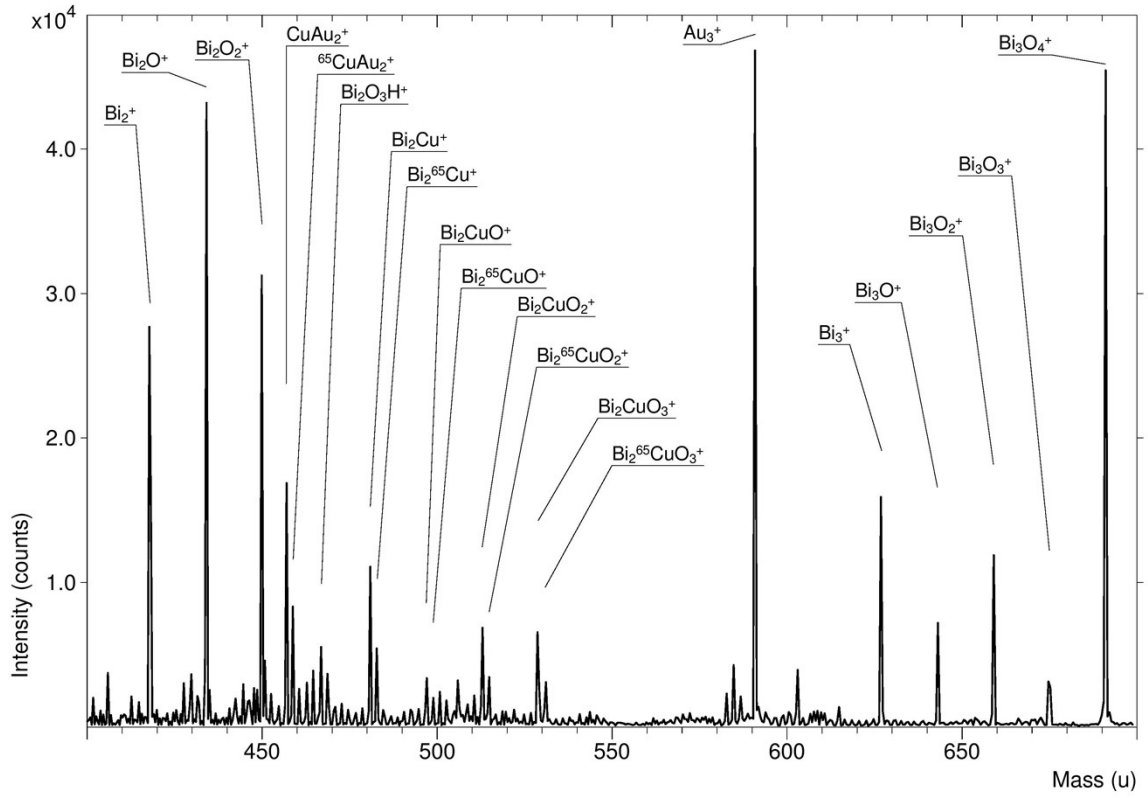
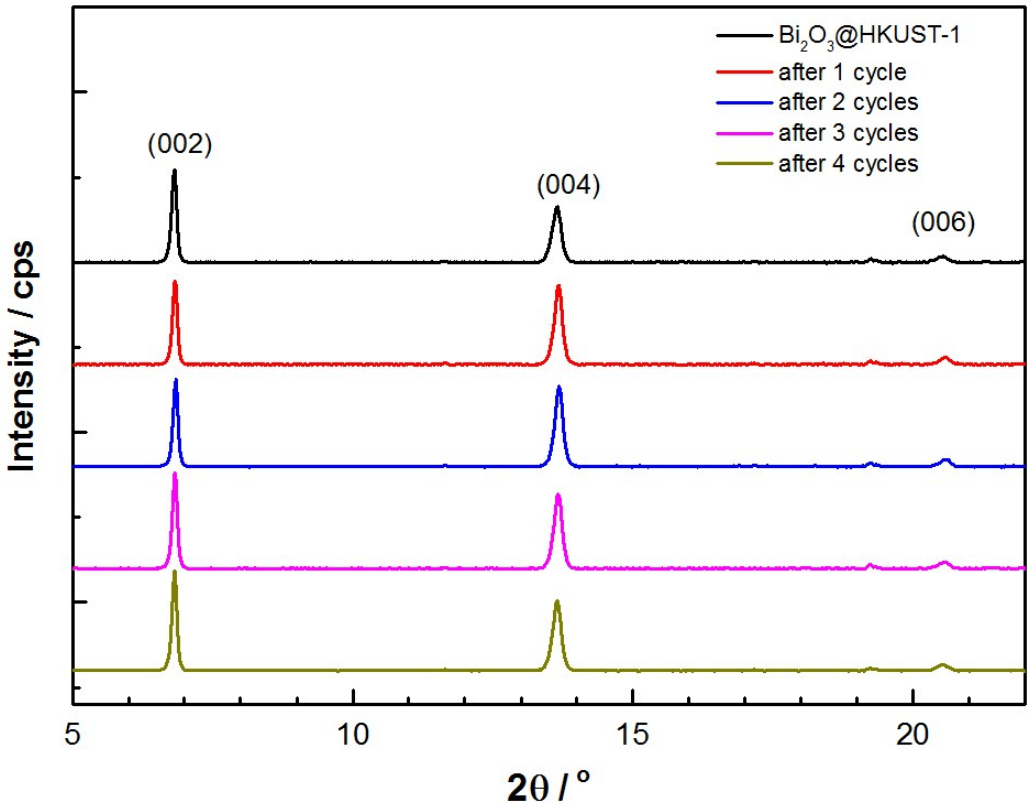


Figure S11. Dynamic SIMS of a Bi_2O_3@HKUST-1 SURMOF stack performed with C_{60} (20 keV, 0.1 pA) bunched analysis beam and O_2 (500 eV, 110 nA) sputter beam. 400 < m/z < 700.

Under dynamic SIMS conditions, using a high current oxygen sputter beam to erode the surface of a Bi_2O_3@HKUST-1 SURMOF stack gold peaks from the substrate appear and new cluster ions like $CuAu_2$ are formed due to the mixing process during ion bombardment.

Table S1: SAED (Selected Area Electron Diffraction) data and lattice spacing (d) for comparison between electron diffraction and XRD data of [111] oriented HKUST-1.

	SAED d [nm]	*HKUST [111] d [nm]*			
			H	K	L
	0.915	0.930	2	2	0
	0.547	0.537	2	2	4
	0.470	0.465	4	4	0
	0.359	0.351	2	4	6
	0.310	0.310	6	6	0
	0.265	0.268	4	4	8
	0.222	0.213	6	4	10



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155 Figure S12. XRD patterns for Bi_2O_3@HKUST-1 SURMOF before and after reaction.

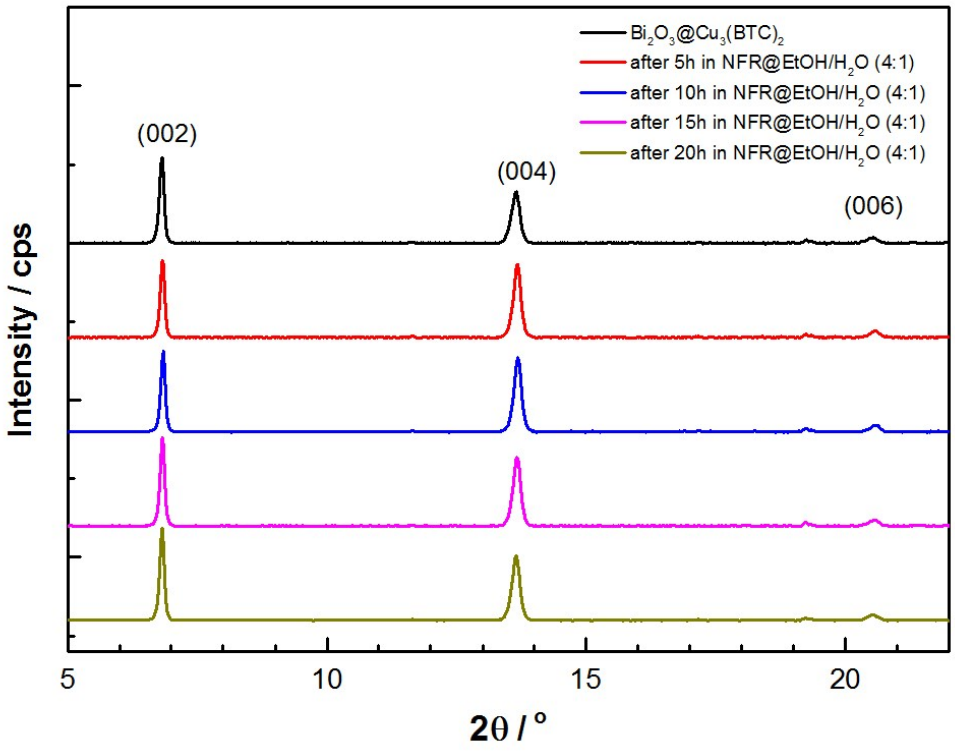

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Figure S13. XRD patterns for Bi_2O_3@HKUST-1 SURMOF in NFR@EtOH/H_2O solution for different times.

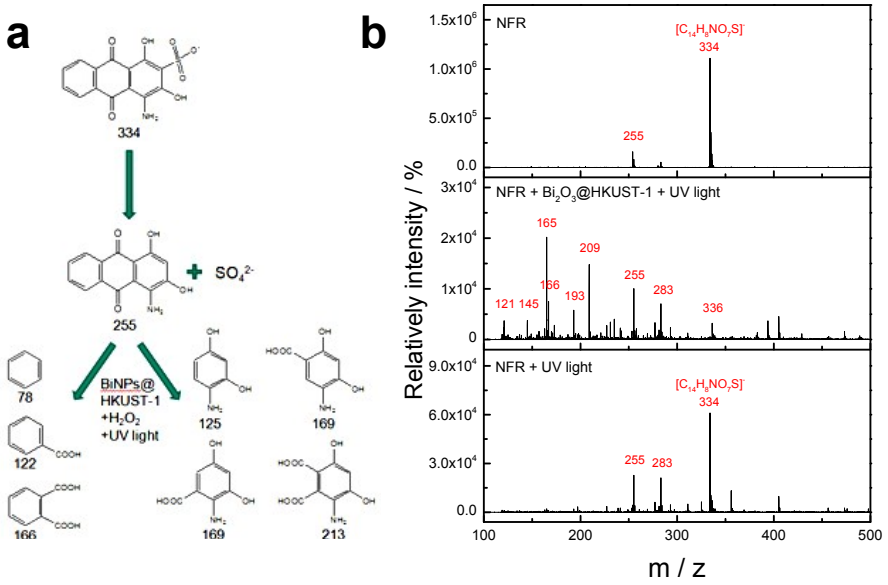

Figure S14. (a) Proposed degradation pathway of NFR using the Bi_2O_3@ HKUST-1 SURMOF for the photodegradation of NFR under UV light irradiation. (b) ESI-MS of the NFR solution (top), NFR solution after UV light exposure with Bi_2O_3@HKUST-1 SURMOF (middle), and NFR solution after UV light exposure without any catalyst (bottom).

As shown in Figure S14, the application of the Bi_2O_3@HKUST-1 SURMOF catalysis system leads to an efficient photodegradation of the parent compound, NFR, and to an enhanced formation of smaller photodegradation products.

References

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