Electronic Supplementary Material (ESI) for Nanoscale.

Supporting Material Information

MOF-Templated Synthesis of 3D Bi_2O_3 Supracrystals with Bcc Packing

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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 up from 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. Predeuteratedhexadecanethiol SAM on Au/Ti/Silicon substrates were used for reference measurements.

Raman spectra were measured using a Bruker Senterra Raman microscope (Bruker Optics, Ettlingen, GER), equipped with an 50x Olympus MPLAN objective NA 0.45 and a frequency doubled DPSS NdYAG-Laser, λ=532nm, operated at 200µW output power. Each spectrum was measured with 180 sec integration-time using 3 coadditions (3*60 sec). For data acquisition as well as spectra evaluation Bruker OPUS software Ver 7.5 was used.

Scanning electron microscope (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.

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 SURMOF. For TEM measurement, samples were prepared by remove the SURMOF 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).

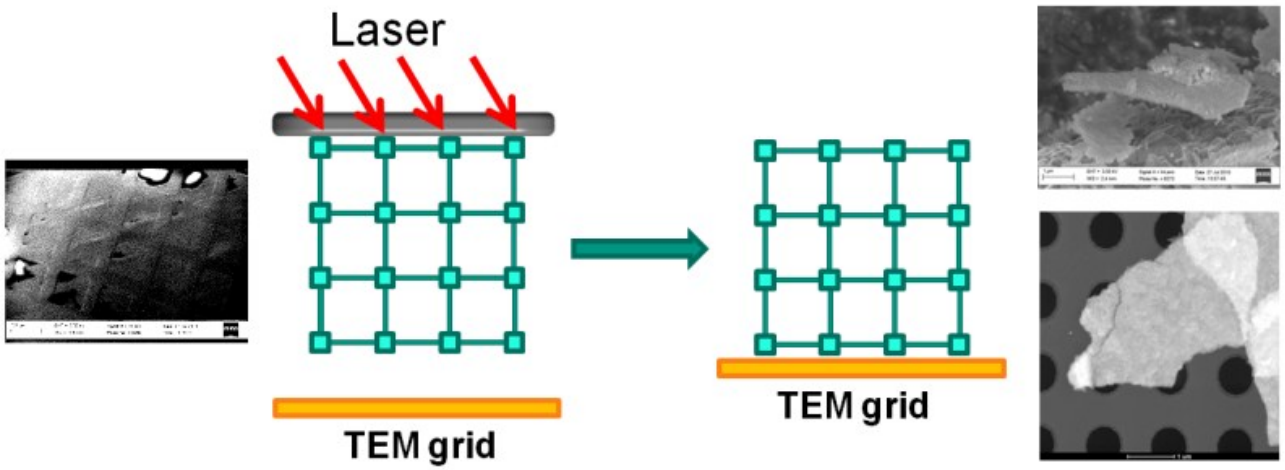

Figure S1 Synthesis scheme of the SURMOFs TEM sample preparation.

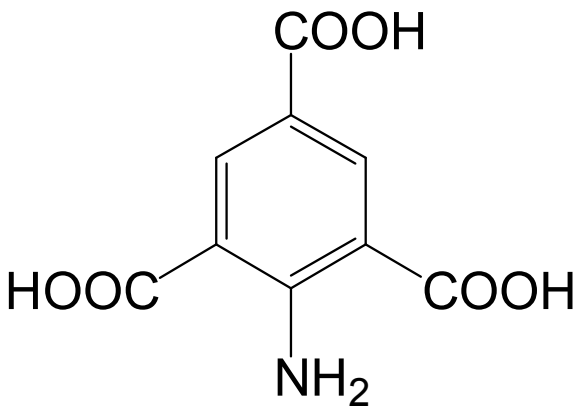

Figure S2 The structure formula of NH_2-BTC molecule.

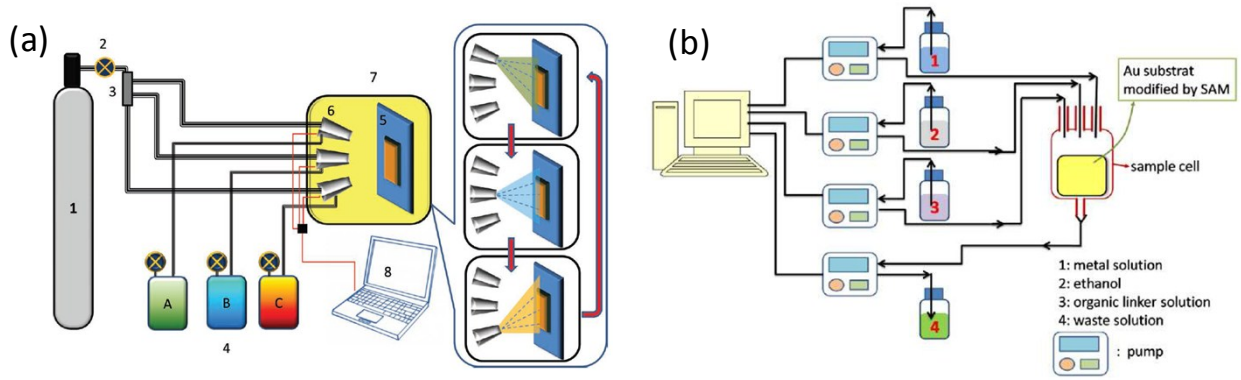

Figure S3 (a) schematic of the setup employed for the fabrication of MOF thin films with the spray method: (1) Gas supply, (2) gas flow controller (3) three-way valve gas distributor (4) (A, B, C) solutions storage containers (5) sample holder (6) dosing valves, (7) spray chamber, (8) PC (Figure taken from Ref.[32]). (b)Schematic diagrams for the automated LBL growth of MOFs thin films on substrates functionalized with SAMs. The preparation is done by repeated immersion cycles first in solution of the metal precursor and subsequently in the organic ligand solution, with solvent rinsing in between (Figure taken from Ref.[29]).

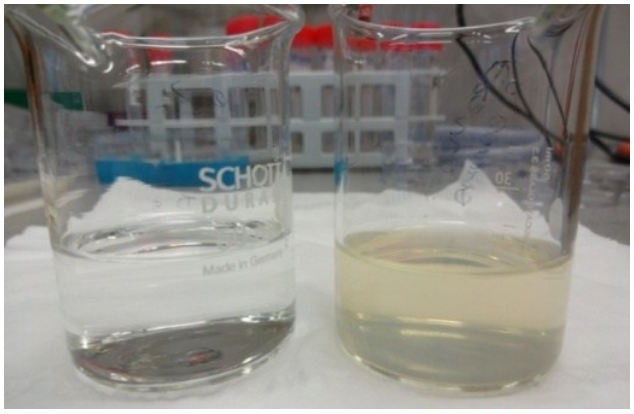

Figure S4 $BiPh_3$ ethanol solution without irradiation (left) and after irradiation (right)

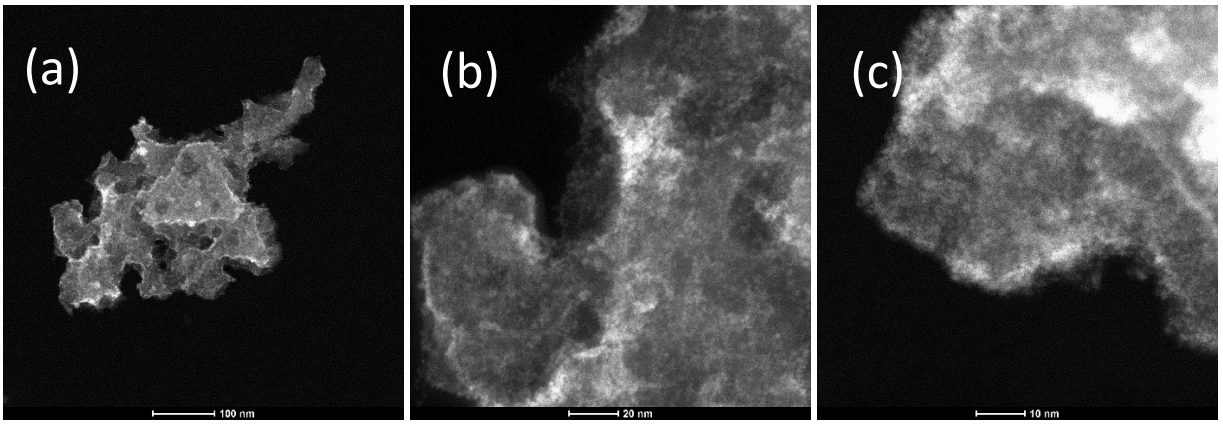

Figure S5 (a-c) HAADF-STEM image of Bi_2O_3@$Cu_3(NH_2\text{-}BTC)_2$ SURMOFs.

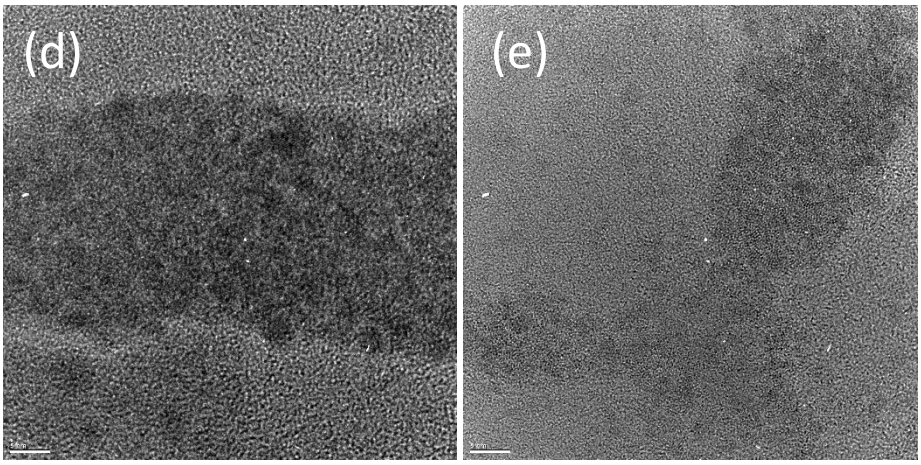

Figure S5 (d-e) HR-TEMs image of Bi_2O_3@$Cu_3(NH_2\text{-}BTC)_2$ SURMOFs.

Table S1: hkl and d-values from HKUST-1 MOF powder XRD in comparison to SAED (Selected Area Electron Diffraction with 4% calibration tolerance) patterns measured of Bi_2O_3@$Cu_3(NH_2\text{-}BTC)_2$ SURMOFs thin films, See Fig.S5b.

h	k	l	d	°2th [Cu K_alp]	rel. Int.
1	1	1	15.20664	5.80716	0.4
0	0	2	13.16934	6.70649	11.6
0	2	2	9.31213	9.48984	28.6
3	1	1	7.94141	11.13262	2.1
2	2	2	7.60332	11.62931	100.0
0	0	4	6.58467	13.43609	35.9
3	3	1	6.04251	14.64798	7.4
0	4	2	5.88951	15.03068	7.7
4	2	2	5.37636	16.4748	13.4
3	3	3	5.06888	17.48177	14.9
5	1	1	5.06888	17.48177	14.9
0	4	4	4.65606	19.04556	53.1

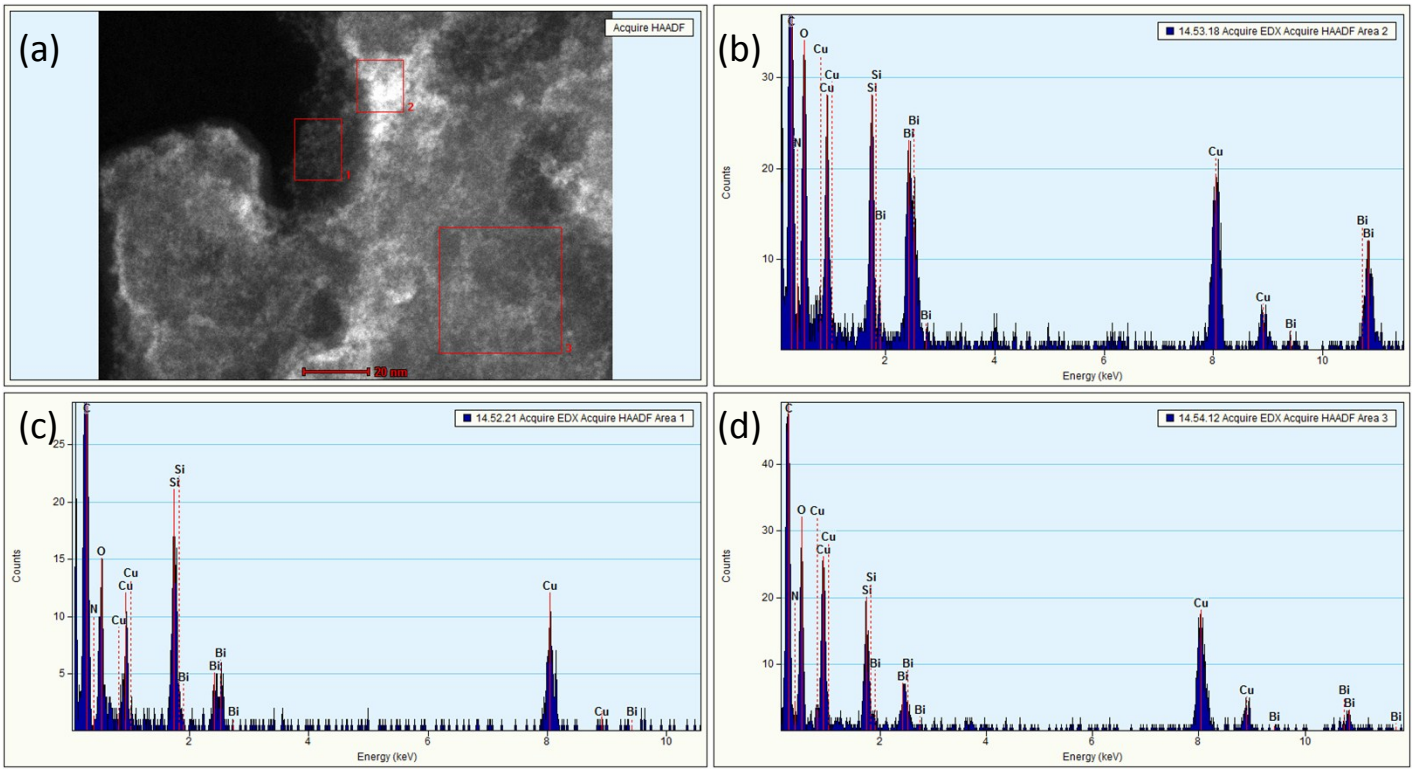

Figure S6a-d Example EDX analysis in different areas of Bi_2O_3@$Cu_3(NH_2\text{-}BTC)_2$ SURMOFs flakes.

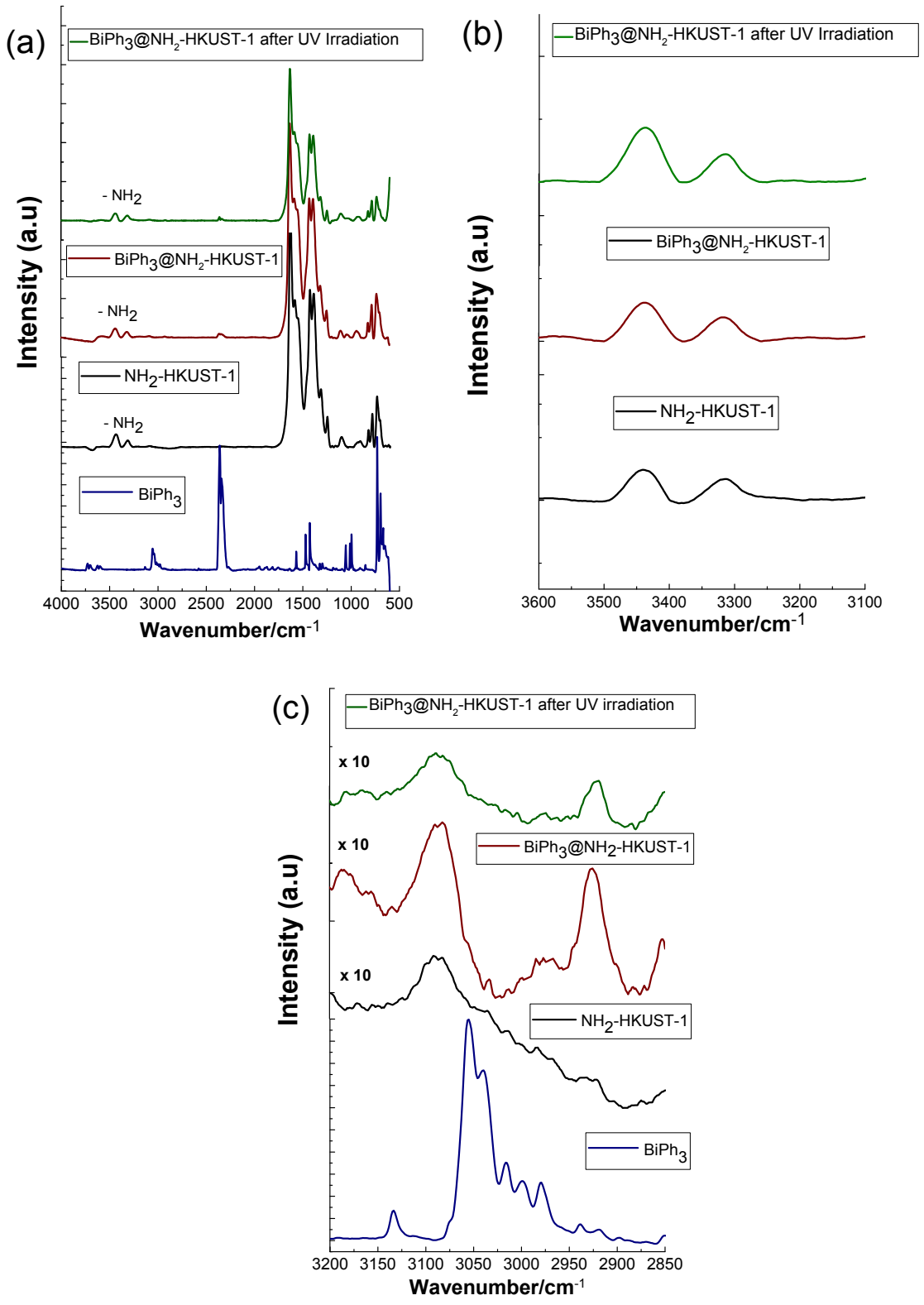

Figure S7a and c: IR spectrum for $BiPh_3$ (blue), $Cu_3(NH_2\text{-}BTC)_2$ (black), $Cu_3(NH_2\text{-}BTC)_2$ after loading $BiPh_3$ (red) and after UV light irradiation (green). b: IR spectrum, zoom in of the characteristic -NH_2 stretching vibrations.

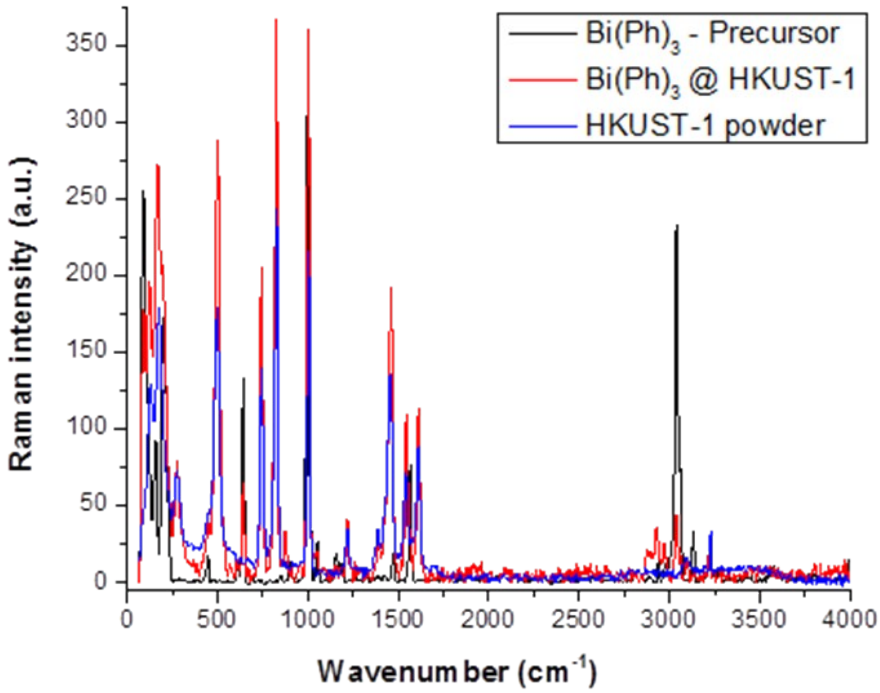

Figure S8a Raman spectrum of HKUST-1 powder, $Bi(Ph)_3$ precursor and HKUST-1@$Bi(Ph)_3$ loaded powders.

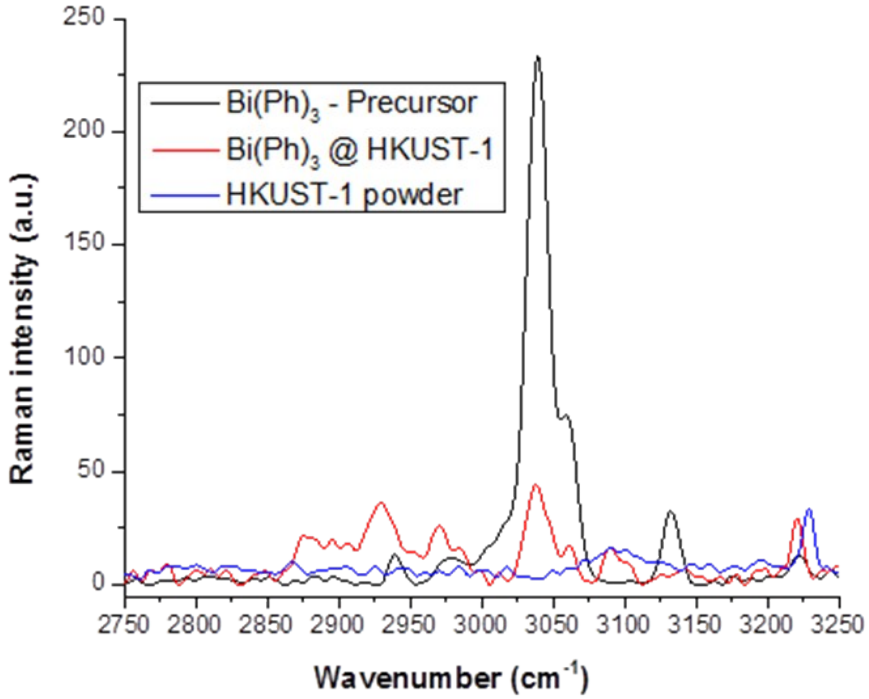

Figure S8b Raman spectrum of HKUST-1 powder, $Bi(Ph)_3$ precursor and HKUST-1@$Bi(Ph)_3$ loaded powders in the range from 2750 to 3250 cm^{-1}.

Raman measurements could not be performed on the SURMOFs thin films due to the low signal intensity. However, HKUST-1 powders as well as $Bi(Ph)_3$@HKUST-1 powders have been characterized by Raman spectroscopy, see Fig.S8a-b. Additional bands from the loaded $Bi(Ph)_3$ precursor can be observed from 2850 to 3100 cm^{-1} in the Raman spectrum, (see Fig.S8b) resulting from phenyl ring vibrations of the loaded $BiPh_3$ precursor. Furthermore, an increase in the intensity ratio of the bands in the range of 250-450 cm^{-1} as well as band in the range of 1200-1700 cm^{-1} in the Raman spectrum was observed, after $Bi(Ph)_3$ loading. This is an additional indicator for a successful intercalation/loading of the $Bi(Ph)_3$ precursor into the open MOF network.