

## **Supporting Information**

### **Photoinduced Delamination of Metal-Organic Framework Thin Films by Spatioselective Generation of Reactive Oxygen Species**

Xiaojing Liu,<sup>[a]</sup> Antoine Mazel,<sup>[b]</sup> Stefan Marschner,<sup>[c]</sup> Zhihua Fu,<sup>[a]</sup> Marius Muth,<sup>[a]</sup> Frank Kirschhöfer,<sup>[a]</sup> Gerald Brenner-Weiss,<sup>[a]</sup> Stefan Bräse,<sup>[c],[d]</sup> Stéphane Diring,<sup>[b]</sup> Fabrice Odobel,<sup>[b]</sup> Ritesh Haldar,<sup>\*,[a],[c]</sup> Christof Wöll<sup>\*,[a]</sup>

<sup>[a]</sup>Karlsruhe Institute of Technology (KIT), Institute of Functional Interfaces (IFG), Hermann-von-Helmholtz Platz-1, 76344 Eggenstein-Leopoldshafen (Germany)

E-mail: [ritesh.haldar@kit.edu](mailto:ritesh.haldar@kit.edu); [christof.woell@kit.edu](mailto:christof.woell@kit.edu).

<sup>[b]</sup>Université de Nantes, CNRS, CEISAM UMR 6230, F-44000, Nantes, France

<sup>[c]</sup>Karlsruhe Institute of Technology (KIT), Institute of Organic Chemistry (IOC), Fritz-Haber Weg 6, 76131 Karlsruhe (Germany)

<sup>[d]</sup>Karlsruhe Institute of Technology (KIT), Institute of Biological and Chemical Systems (IBCS-FMS), Hermann-von-Helmholtz Platz-1, 76344 Eggenstein-Leopoldshafen (Germany)

<sup>[e]</sup>Tata Institute of Fundamental Research Hyderabad, Gopanpally, Hyderabad-500046, Telangana, India

Email: [riteshhaldar@tifrh.res.in](mailto:riteshhaldar@tifrh.res.in); [christof.woell@kit.edu](mailto:christof.woell@kit.edu)

**Experimental section:****Materials:**

Zinc acetate dihydrate (Merck Millipore), ethanol (VWR, Germany)

The silicon substrates with a [100] orientation are from Silicon Sense (US). The quartz glasses are from Alfa Aesar. These substrates were treated with plasma (Diener Plasma) under O<sub>2</sub> (50 sccm) for 30 min to remove the impurities and generated a surface with hydroxyl groups. All the linkers are synthesized according to the previously reported procedures.<sup>1-3</sup>

**Fabrication of Zn-PPY SURMOF-2 structure:**

Ethanolic solution of 1 mM zinc acetate and 20  $\mu$ M of PPY ethanolic solutions were sequentially deposited onto the precleaned Si/SiO<sub>2</sub> or quartz substrates using spin coating method in a layer-by-layer fashion. After the metal or linker coating, the samples were rinsed with ethanol to remove unreacted metal/linker or by-products from the surface. For metal and linker both, the spin coating time is fixed as 10 s with rpm of 2000.

**Fabrication of MOF-on-MOF Zn-PPY-TPE structure:**

To fabricate Zn-PPY-TPE thin films, first 30 cycle Zn-PPY film was deposited and then 20 cycle of Zn-TPE film was deposited. The deposition methodology is similar to that for only Zn-PPY SURMOF growth. For Zn-PPY structure, instead of PPY linker a 20  $\mu$ M of TPE ethanolic solution was used.

**Fabrication of trilayer layer structure:**

On top of the Zn-PPY-TPE structure, the target layer Zn-cNDI was deposited in a similar fashion as in for the pristine SURMOF fabrication.

**X-ray diffraction (XRD):** The XRD measurements for out-of-plane (co-planar orientation) were carried out using a Bruker D8-Advance diffractometer equipped with a position sensitive detector Lynxeye in geometry, variable divergence slit and 2.3° Soller-slit was used on the secondary side. The Cu-anodes which utilize the Cu K $\alpha$  1,2-radiation ( $\lambda$  = 0.154018 nm) was used as source.

**UV-Vis spectroscopy:** The ultraviolet–visible spectra were recorded by a Cary5000 spectrometer with a UMA unit from Agilent.

**Liquid chromatography-Mass spectrometry method:**

The liquid chromatography tandem mass spectroscopy (LC-MS) system consisted of an Agilent 1100 high performance liquid chromatograph (HPLC) with a Gemini C18 110 Å column (30×2 mm, 3 µm particle size) connected to an ABSciex X500R QTOF mass spectrometer with an IonDrive TurboV-source for HPLC/ESI-QTOF-MS analysis. The mobile phases for HPLC separation are acetonitrile + 0.1 % (v/v) formic acid (A) and water + 0.1 % (v/v) formic acid (B) at a flow rate of 0.5 mL/min. The initial mobile phase condition was 20 % A running for 5 min and then 80 % A. Afterwards the initial condition of 20 % A ran for 1 min to equilibrate the column. The injection volume of mobile phased was 20 µL.

Porphyrin and cNDI were analyzed in positive mode, and TPE was analyzed in negative mode.

In order to study the component of exfoliated samples, the samples were dissolved in 10 % acetic acid in ethanol with sonication for 10 min sonication.

Table S1: list of compounds and observed mass data

species	elemental composition	m/z observed
TPE	C <sub>40</sub> H <sub>28</sub> O <sub>4</sub>	571.191
Ox-TPE	C <sub>20</sub> H <sub>14</sub> O <sub>3</sub>	301.088
cNDI	C <sub>52</sub> H <sub>60</sub> N <sub>4</sub> O <sub>8</sub>	869.453
PPY	C <sub>46</sub> H <sub>30</sub> N <sub>4</sub> O <sub>4</sub>	701.218

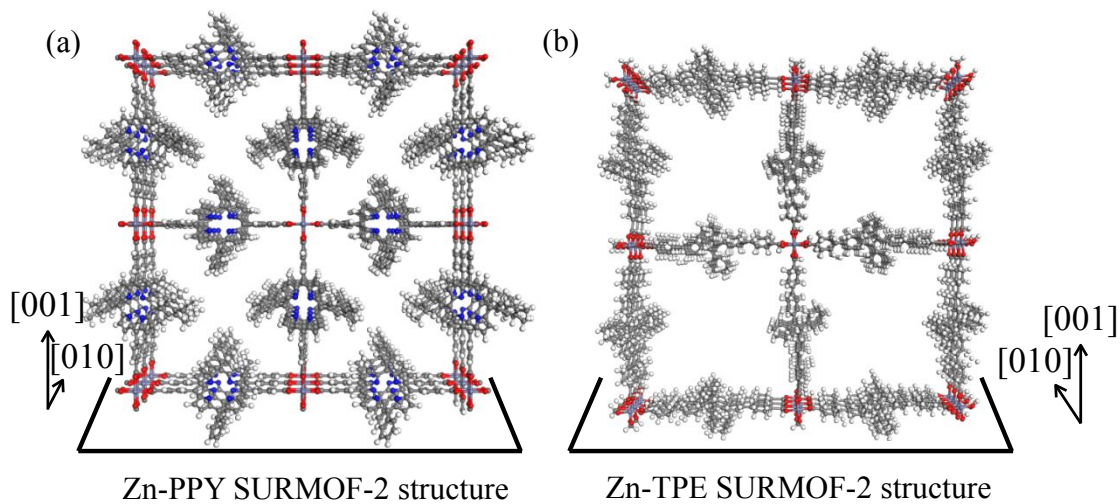
**Atomic Force Microscopy measurements:**

The surface topography and conductivity test were performed with the Bruker's Dimension® Icon™ SPM system under the air atmosphere.

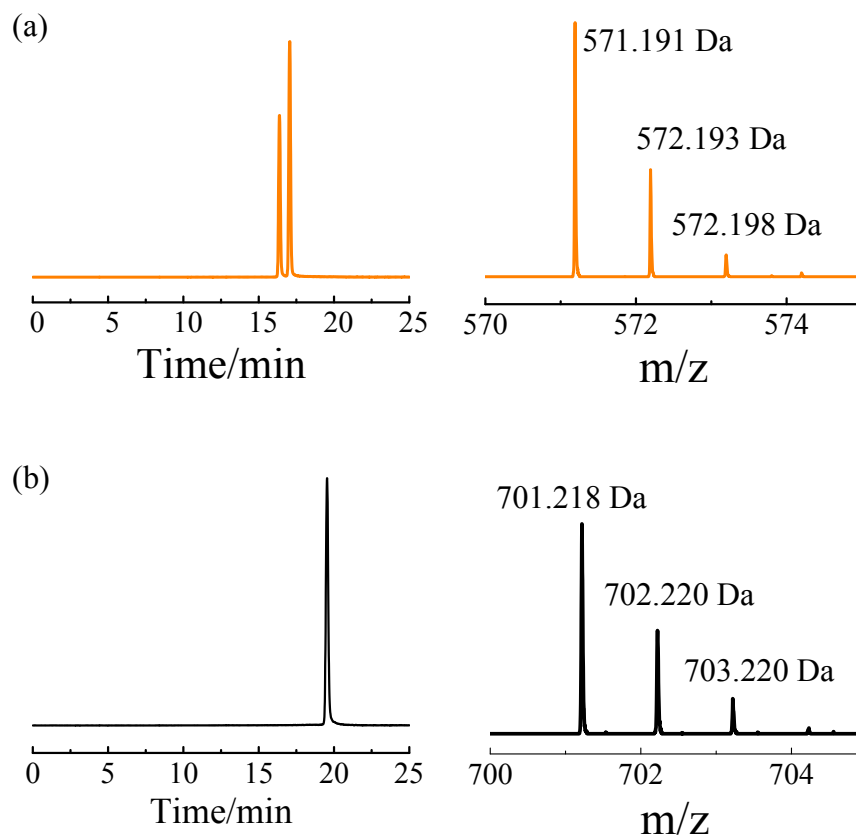
For the topography experiments, silicon substrates were used. The topography process was performed in the ScanAsyst in air mode (cantilever type: ScanAsyst in air) with a force (~5 nN) of the tip on the surface. During the scanning process (scan rate: 1 Hz, number of lines: 256), the topography of MOF nanosheets were obtained.

For the conductive AFM experiments, gold substrates were used. The conductivity measurements (PFTUNA probes) were investigated by the PeakForce TUNA™ method of the Bruker's

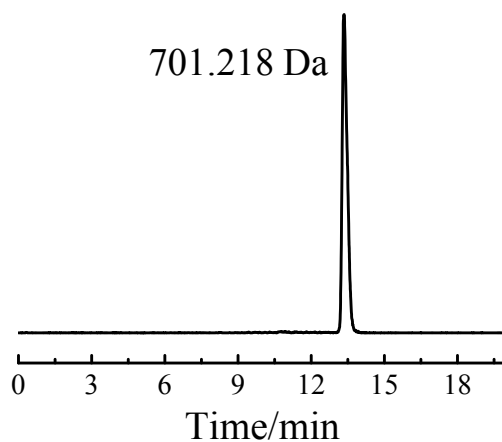
Dimension® Icon™ SPM system. In the ramp process with ramp range from -500 mV to 500 mV (Ramp rate: 1 Hz), the current sensitivity was set to highest sensitivity available (1 nA). The current was read out at a force of 66 nN.



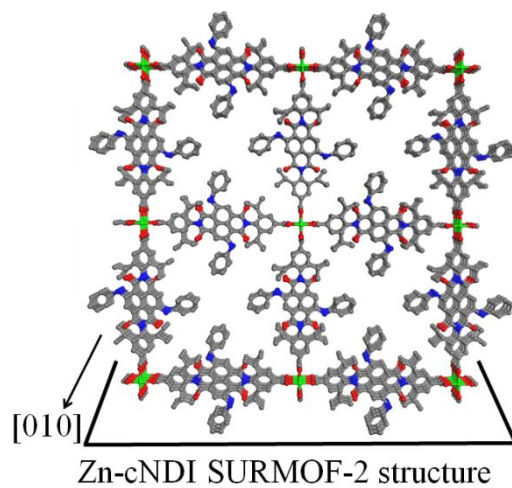
**Figure S1:** SURMOF-2 structure of (a) Zn-PPY and (b) Zn-TPE.



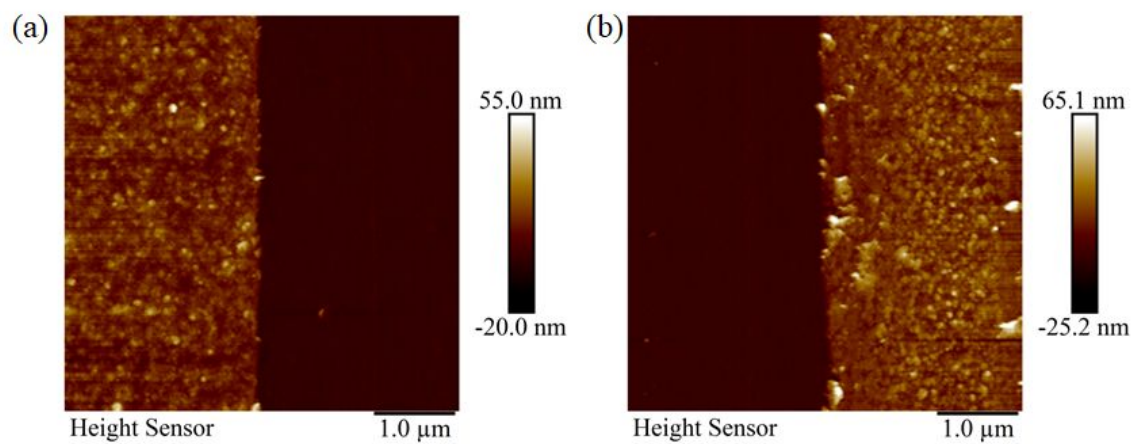
**Figure S2:** LC-MS profiles and isotopic mass distribution of the photo irradiated solution of 1:1 PPY+TPE mixture: (a) in negative ion mode (orange) (b) in positive ion mode.



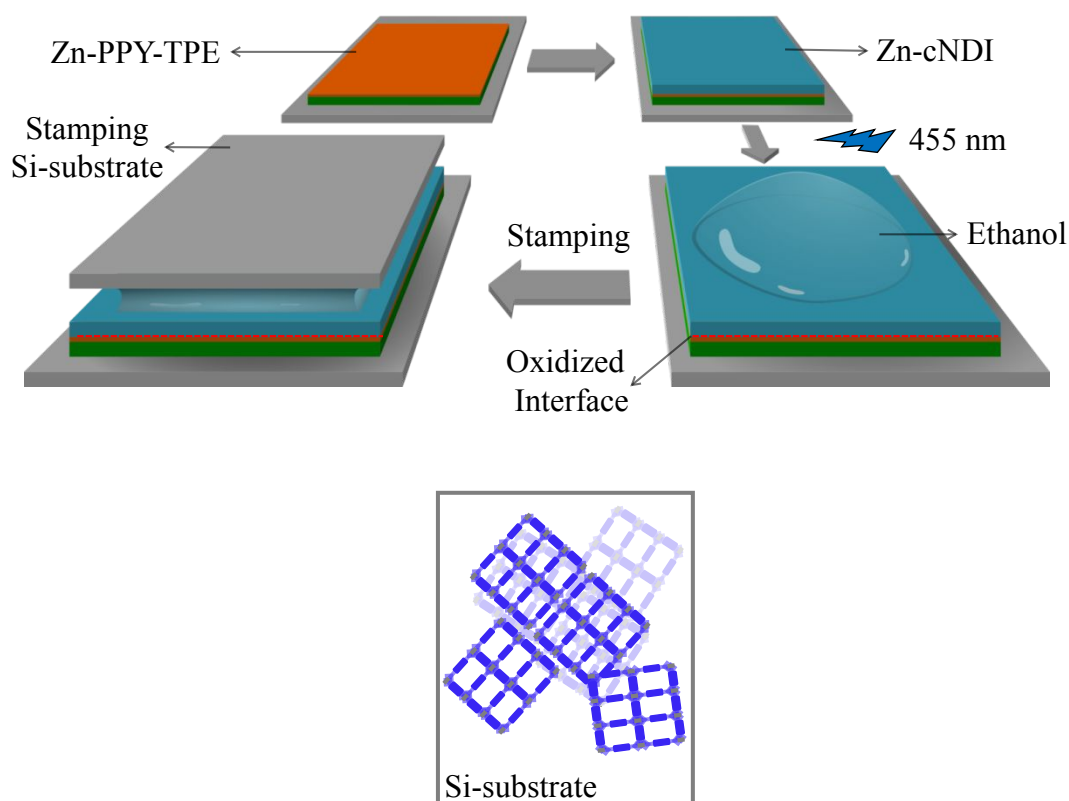
**Figure S3:** LC-MS profile of the dissolved Zn-PPY-TPE layer (dissolved by 5% acetic acid in ethanol) in positive ion mode showing characteristic retention time of PPY.



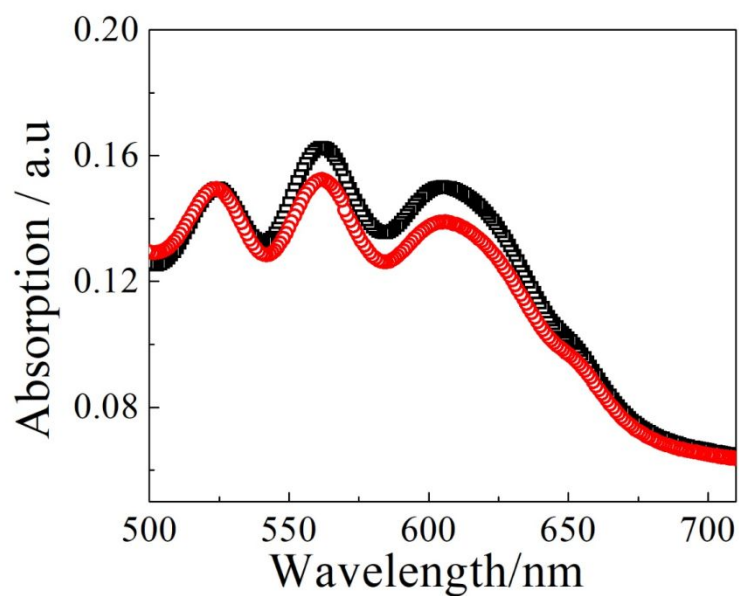
**Figure S4:** SURMOF-2 structure of Zn-cNDI.



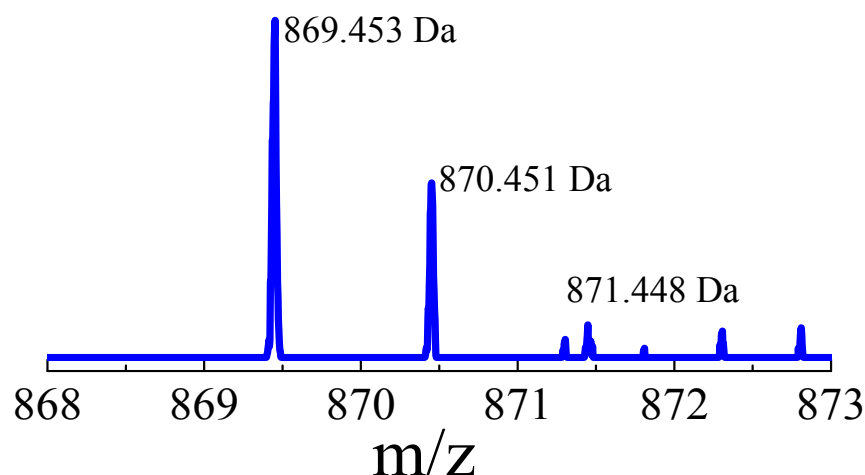
**Figure S5:** AFM images of the (a) Zn-cNDI and (b) Zn-PPY-TPE SURMOFs.



**Figure S6:** A schematic of the detached layer transfer process by a stamping method. Procedure is also discussed in the main text.



**Figure S7:** Absorption spectra of the Zn-PPY-TPE-cNDI before (black) and after (red) detachment of top layer.



**Figure S8:** Isotopic mass distribution of cNDI in the delaminated Zn-cNDI structure.

1. Liu, J.; Zhou, W.; Liu, J.; Howard, I.; Kilibarda, G.; Schlabach, S.; Coupry, D.; Addicoat, M.; Yoneda, S.; Tsutsui, Y.; Sakurai, T.; Seki, S.; Wang, Z.; Lindemann, P.; Redel, E.; Heine, T.; Wöll, C., Photoinduced Charge-Carrier Generation in Epitaxial MOF Thin Films: High Efficiency as a Result of an Indirect Electronic Band Gap? *Angewandte Chemie International Edition* **2015**, 54 (25), 7441-7445.
2. Haldar, R.; Diring, S.; Samanta, P. K.; Muth, M.; Clancy, W.; Mazel, A.; Schlabach, S.; Kirschhöfer, F.; Brenner-Weiß, G.; Pati, S. K., Enhancing selectivity and kinetics in oxidative photocyclization by supramolecular control. *Angewandte Chemie International Edition* **2018**, 57 (41), 13662-13665.
3. Haldar, R.; Chen, H.; Mazel, A.; Chen, D. H.; Gupta, G.; Dua, N.; Diring, S.; Odobel, F.; Wöll, C., Antenna Doping: The Key for Achieving Efficient Optical Wavelength Conversion in Crystalline Chromophoric Heterolayers. *Advanced Materials Interfaces* **2021**, 8 (10), 2100262.