Supplement information

**MOF-on-MOF Heteroepitaxy: Perfectly oriented \([\text{Zn}_2(\text{ndc})_2(\text{dabco})]_n\) grown on \([\text{Cu}_2(\text{ndc})_2(\text{dabco})]_n\) thin films**

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S1. AFM measurements

The AFM images shown in Fig. S1a were recorded at ambient conditions using a Multimode Nanoscope IIIa (Digital Instruments) equipped with a J scanner and operated in tapping mode using Arrow TM NC tips (tip radius<10 nm, NanoWorld AG, Schwitzer-land). The AFM images shown in Fig. S1b were performed with a commercial AFM (5500 AFM, Agilent Technologies) operating in AAC mode. A calibration silicon grating was used to calibrate the piezo scanner. Both topological and phase images were recorded under ambient conditions (air environment and room temperature) with scan rates less than 1 Hz, collecting 512 X 512 points for each image. The commercial rectangular silicon cantilevers from Olympus have nominal spring constants in the range of 2–3 N/m with a resonance frequency of 73–82 kHz, and in the range of 49–77 N/m with a resonance frequency of 316–364 kHz. The MOF thin films on Au substrates were fixed on the sample stage and cantilever was carefully approached on the crystal surface.

Figure S-1a. (left) AFM image of Cu$_2$(ndc)$_2$(dabco) MOF (50 cycles) grown on a SAM laterally patterned by micro-contact printing (µCP) consisting of pyridine-terminated squares and CH$_3$-terminated stripes. (right) AFM image of Cu$_2$(ndc)$_2$(dabco) MOF (50 cycles) grown on a pyridine terminated SAM.
Figure S-1b. (left) AFM image of Cu_{2}(ndc)_{2}(dabco) MOF (60 cycles) grown on a pyridine terminated SAM.(right) AFM image of Zn_{2}(ndc)_{2}(dabco) MOF (50 cycles) grown on Cu_{2}(ndc)_{2}(dabco) MOF (60 cycles).
S2. Synchrotron X-ray diffraction measurement

Synchrotron X-ray measurements were performed with a four-circle diffractometer having $\phi$, $\chi$, $\theta$, and $2\theta$ circles at beamline BL13XU for surface and interface structures, SPring-8 as illustrated in Figure S-3. The $\phi$, $\chi$, and $\theta$ angles are for orienting a sample; in addition, $2\theta$ is for orienting an x-ray detector. The $\theta$ angle is the outermost circle with the horizontal axis of rotation coincident with that of $2\theta$. The $\chi$ circle is mounted on the $\theta$ circle. The $\chi$ axis of rotation is perpendicular to the $\theta$ axis and parallel to the incident X-ray beam. The $\phi$ circle is mounted on the $\chi$ circle, with its axis of rotation which lies in the plane of the $\chi$ circle. An X-ray beam (100 $\times$ 100 $\mu$m$^2$) was incident on the sample. Si-PIN photo-diode and Oxford scintillation detectors were used for the measurement. The MOF thin film on Au substrate was fixed on the sample stage. The measurement was carried out under Helium gas condition. For each sample, the $\theta$-$2\theta$ scan at the initial position ($\chi = 90^\circ$) was carried out to determine the orientation of the crystal, and then the angles of $\phi$, $\chi$, $\theta$, and $2\theta$ were moved to the desired Brag position and a scan of the vertical orientation angle of the sample was performed.

Figure S-2. The schematic drawing of the four-circle diffractometer at beamline BL13XU for surface and interface structures, SPring-8