

Electronic Supplementary Information

[001]-Oriented Heteroepitaxy for Fabricating Emissive Surface Mounted Metal-Organic Frameworks

Tonghan Zhao,^{*a} Narjes Taghizadeh Rahaghi,^b Jan C. Fischer,^{a,c} Bryce S. Richards,^{a,c} and Ian A. Howard^{*†a,c}

^a Institute of Microstructure Technology, Karlsruhe Institute of Technology, Hermann-von-Helmholtz-Platz 1, 76344 Eggenstein-Leopoldshafen, Germany. Email: tonghan.zhao@kit.edu; iahoward@gmail.com

^b Institute of Solid State Physics, NAWI Graz, Graz University of Technology, Petersgasse 16, A-8010 Graz, Austria.

^c Light Technology Institute, Karlsruhe Institute of Technology, Engesserstrasse 13, 76131 Karlsruhe, Germany.

† Present address: Carl Zeiss AG – Innovation Hub Karlsruhe, Hermann-von-Helmholtz-Platz 6, 76344 Eggenstein-Leopoldshafen

Supplementary Figures

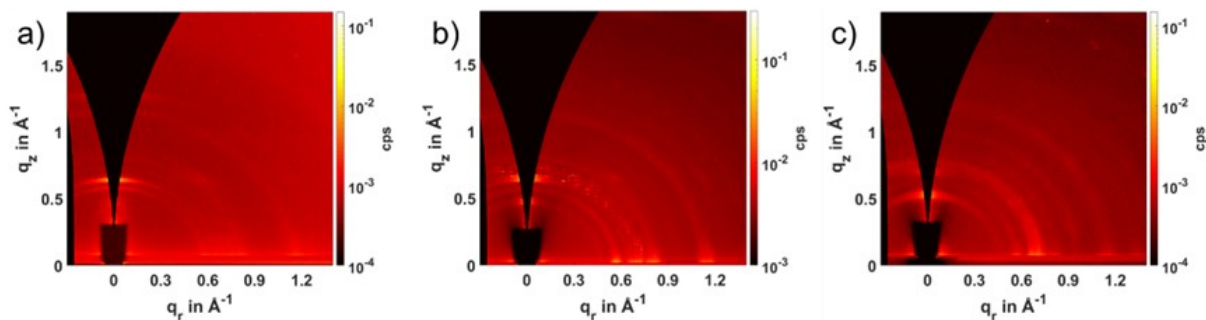


Fig. S1 2D GIWAXS pattern of $(\text{Zn})_2(\text{BDC})_2(\text{DABCO})$ on (a) $\text{TiO}_2@\text{Si}$, (b) $\text{Gd}_2\text{O}_3@\text{Si}$, and (c) glass substrates.

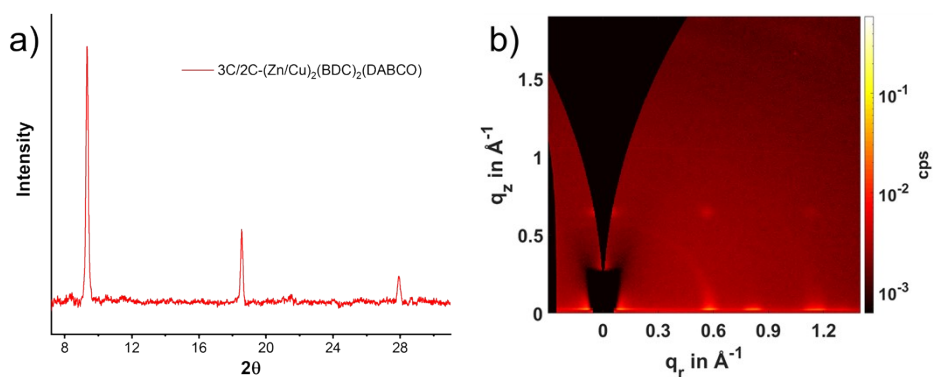


Fig. S2 (a) Out-of-plane XRD pattern and (b) 2D GIWAXS pattern of $3\text{C}/2\text{C}-(\text{Zn}/\text{Cu})_2(\text{BDC})_2(\text{DABCO})$.

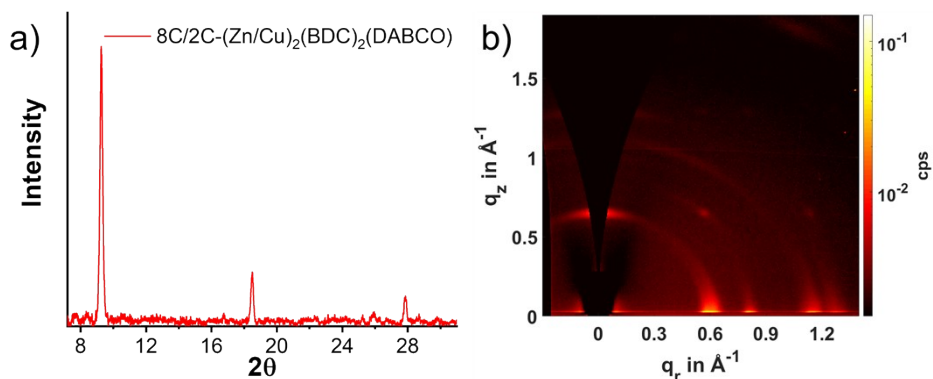


Fig. S3 (a) Out-of-plane XRD pattern and (b) 2D GIWAXS pattern of $8\text{C}/2\text{C}-(\text{Zn}/\text{Cu})_2(\text{BDC})_2(\text{DABCO})$.

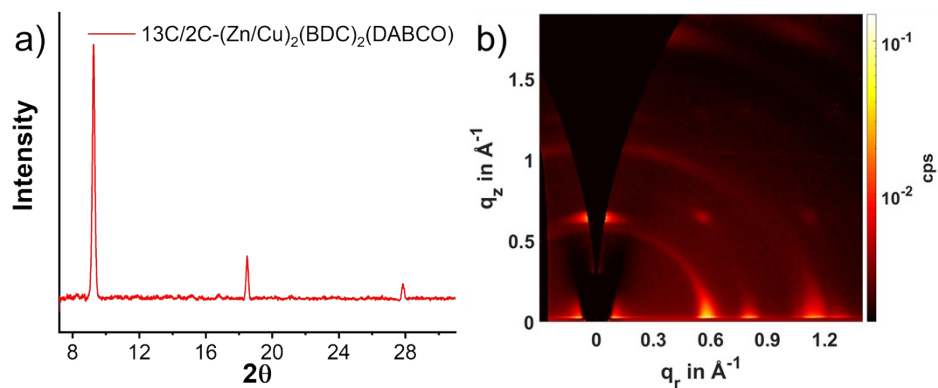


Fig. S4 (a) Out-of-plane XRD pattern and (b) 2D GIWAXS pattern of 13C/2C-(Zn/Cu)₂(BDC)₂(DABCO).

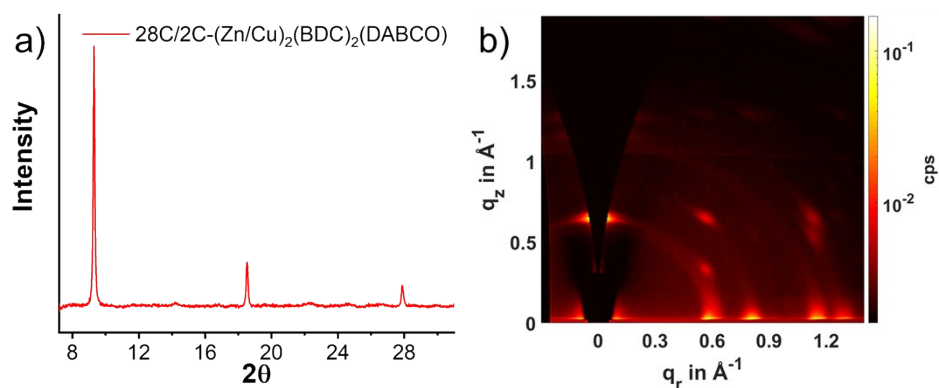


Fig. S5 (a) Out-of-plane XRD pattern and (b) 2D GIWAXS pattern of 28C/2C-(Zn/Cu)₂(BDC)₂(DABCO).

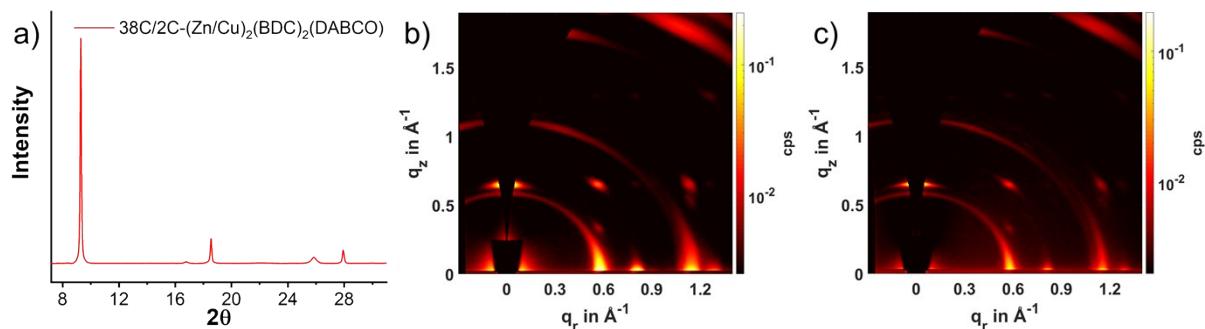


Fig. S6 (a) Out-of-plane XRD pattern and (b and c) 2D GIWAXS pattern of 38C/2C-(Zn/Cu)₂(BDC)₂(DABCO) at (b) $\alpha_i = 0.2^\circ$ and (c) $\alpha_i = 0.05^\circ$.

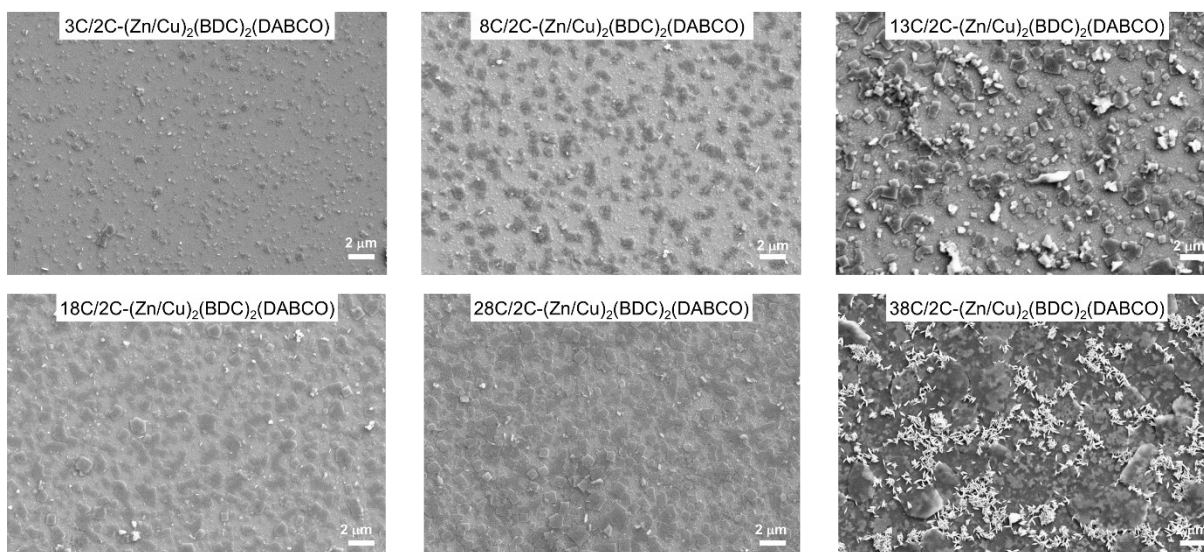


Fig. S7 SEM images of Zn/Cu heterostructures with different growth cycles of $\text{Zn}_2(\text{BDC})_2(\text{DABCO})$ on top of $2\text{C-Cu}_2(\text{BDC})_2(\text{DABCO})$.

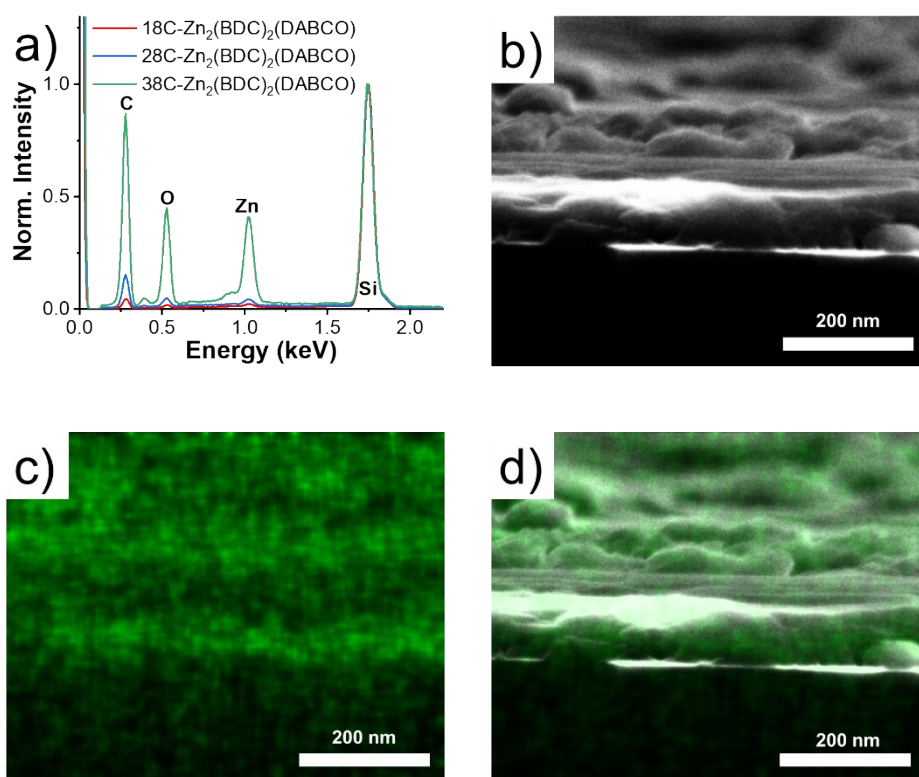


Fig. S8 (a) Normalized EDX spectra of 18C-, 28C-, and 38C- $\text{Zn}_2(\text{BDC})_2(\text{DABCO})$ on top of $2\text{C-Cu}_2(\text{BDC})_2(\text{DABCO})$. (b) Cross-section SEM image of 38C- $\text{Zn}_2(\text{BDC})_2(\text{DABCO})$ on top of $2\text{C-Cu}_2(\text{BDC})_2(\text{DABCO})$. (c) EDX mapping of Zn on the cross-section. (d) Emerged image of (b) and (c).

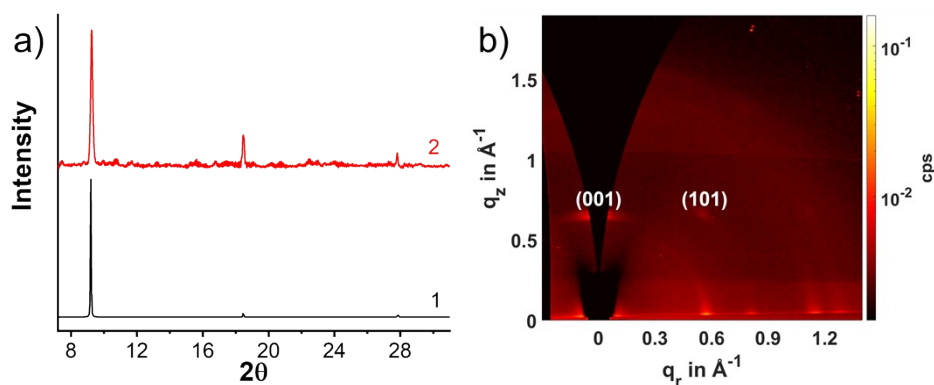


Fig. S9 (a) Out-of-plane XRD pattern of 20C-Zn₂(NDC)₂(DABCO) on top of 2C-Cu₂(BDC)₂(DABCO) and simulated diffractogram of the Zn₂(NDC)₂(DABCO) with preferred orientation along the [001] direction as reference. (b) 2D GIWAXS pattern of 20C-Zn₂(NDC)₂(DABCO) on top of 2C-Cu₂(BDC)₂(DABCO).

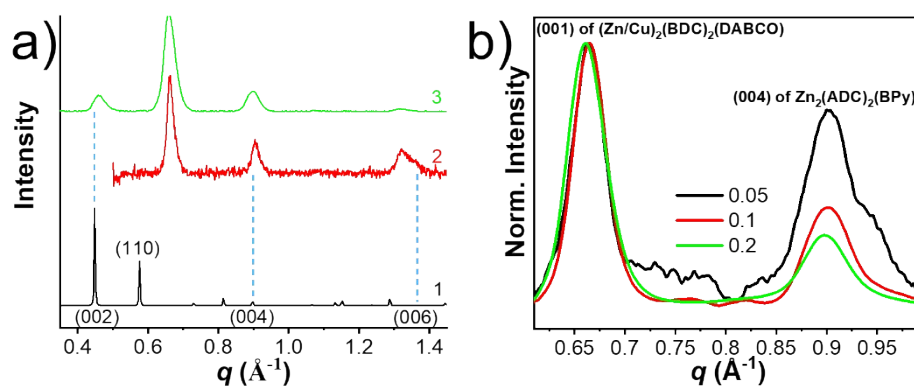


Fig. S10 (a) Out-of-plane XRD pattern (2) and out-of-plane integration result from 2D GIWAXS pattern (3) of 20C-Zn₂(ADC)₂(BPy) on top of 3C/2C-(Zn/Cu)₂(BDC)₂(DABCO) and simulated diffractogram of the Zn₂(ADC)₂(BPy) (1) as reference. (b) GIWAXS out-of-plane plot of 20C-Zn₂(ADC)₂(BPy) on top of 3C/2C-(Zn/Cu)₂(BDC)₂(DABCO) probing at different incidence angles: 0.05°, 0.1°, and 0.2°.

Table S1. Photophysical parameters of Zn₂(ADC)₂(BPy) on 3C/2C-(Zn/Cu)₂(BDC)₂(DABCO), ADC film and ADC in ethanol (5×10^{-7} mol L⁻¹).

	Zn ₂ (ADC) ₂ (BPy) on 3C/2C-(Zn/Cu) ₂ (BDC) ₂ (DABCO)		ADC film	Solvated ADC
λ_{em}^a [nm]	426	501	501	423
τ_1 [ns]	1.23 (54%)	1.79 (52%)	2.15 (52%)	
τ_2 [ns]	6.45 (46%)	7.98 (48%)	6.33 (48%)	
τ^b [ns]	3.62	4.78	4.18	7.11

^a)Excitation with 365 nm;

^b)Mono-exponential fit for ethanolic ADC solution. Bi-exponential fit for Zn₂(ADC)₂(BPy) on

3C/2C-(Zn/Cu)₂(BDC)₂(DABCO) and ADC film, and fluorescence lifetime calculated using the equation $\tau = A_1\tau_1 + A_2\tau_2$.