

ARTICLE

Supporting Information:

Dissolving Uptake-Hindering Surface Defects in Metal-Organic Frameworks

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Supporting Information 1: SURMOF preparation in QCM cell



Figure SI1: Mass density and thickness of HKUST-1 SURMOF during the synthesis. For the experiments shown in Figures 1-3a, the samples are prepared in 90 synthesis cycles, resulting in final SURMOF thicknesses of 122.0 nm (Figure a), 110.1 nm, 112.9 nm and 118.2 nm. The samples, which are used for the experiments shown in Figure 3b, are prepared in 200 synthesis cycles. The SURMOF thicknesses were determined to 520.3 nm, 405.1 nm and 469.4 nm (Figure b).

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Figure SI2: Cyclohexane uptake by the SURMOF relative to the SURMOF mass. The respective treatment is written in the plot.

Supporting Information 3: SURMOF Regeneration at Different Temperatures



Figure SI3: Relative recovery, i.e. the normalized cyclohexane uptake after the water vapor exposure for 1 h and during the ethanol immersion. Ethanol immersion was performed for 138 hours at different temperatures: 65°C (black), 55°C (red) and 45°C (green). In this plot, the final recovery at 45°C and 55°C is assumed to correspond the recovery at 65°C, which is approximately 60%, see Figure SI2.

The determined reaction barrier for annealing the HKUST-1 structure is higher than the activation enthalpy of the BTC binding on copper ions during the step-by-step HKUST-1 SURMOF synthesis.^[7]



Figure SI3-1: Eyring-Polanyi-plot for the temperature dependence of the uptake regeneration. The slope of the linear fit results

$\Delta H^{\,\ddagger} = 93 \pm 11 \frac{kJ}{mol} \, . \label{eq:deltaH}$ in an activation enthalpy of

Supporting Information 4: X-Ray Photoelectron (XPS) Spectroscopy



Figure SI4: XPS data of O1s core level of HKUST-1 after water vapor exposure. Peak position was calibrated to 532.1 eV for carboxylates as described in literatures.^[8] Due to the simple Gaussian peak shape, no indication for H₂O is visible. It should be stated that the spectrum provides no evidence for a distinction between -OH and -COO, i.e. remaining hydroxyl-ions cannot be verified.

Supporting Information 5: Density Functional Theory calculations of the Defect Structure

The DFT calculations were performed in the gas phase by means of the Amsterdam Density Functional (ADF2017) software package.¹ The structures of the molecular complexes were optimized using the well-tested² B3LYP functional³ with the atom pair-wise D3 dispersion correction.⁴ Slater basis sets⁵ of triple-zeta quality with one polarization function (TZP) for all atoms and "good" quality of the Becke integration grid were used. Scalar relativistic corrections were taken into account via the ZORA⁶ formalism. The energy of the copper 2p electronic states were assessed at the same theoretical level.

Model structures **1-3** as tabulated in Table S1 represent regular four-fold copper paddle wheels with and without axial water ligands. Model structures **4-19** represent irregular paddle-wheels (defects) containing not only Cu²⁺, but also Cu⁺ or Cu³⁺ ions, BTC linkers of which one or two are partially or completely detached from the metal node, and one or two intact or dissociated water molecules.

Table S1. Molecular model complexes considered in this study. All structures optimized at the B3LYP-D3/ZORA scalar/TZP level of theory.

No	Complex type	Complex visualization	Chargeª	Multipli city <i>, M</i> ^b	Metal- metal pair with formal oxidati on state	∆E _{Bondi} _{ng} , eV ^c	ΔΕ _{Cu 2p} , eV ^d
1	Cu₂(BTC)₄_ perfect PW		0	3	Cu ²⁺ / Cu ²⁺	N/A	0.0
2	Cu ₂ (BTC) ₄ (H ₂ O)_ perfect PW		0	3	Cu ²⁺ / Cu ²⁺	N/A	0.2

3	Cu ₂ (BTC) ₄ (H ₂ O) ₂ _perfe ct PW		0	3	Cu ²⁺ / Cu ²⁺	N/A	0.0
4	Cu₂(BTC)₄ − (diss-H₂O)	2(BTC) ₄ ss-H ₂ O)	0	3	Cu ²⁺ / Cu ²⁺	0.0	0.2
5				1	Cu*/ Cu ³⁺	+1.6	2.8
6	Cu ₂ (BTC) ₄ (H ₂ O) ^e		0	3	Cu ²⁺ / Cu ²⁺	0.0	0.1

7			1	Cu*/ Cu ³⁺	+1.3	2.3
8	Cu₂(BTC)₄ - (H₂O)₂ ^e	0	3	Cu ²⁺ / Cu ²⁺	0.0	1.0
9		•	1	Cu*/ Cu ³⁺	+1.5	2.5
10	Cu ₂ (BTC) ₄ (OH)_ charged ^e	-2	2	Cu*/ Cu²+	N/A	3.3

11	Cu ₂ (BTC) ₃ (OH)_charge d	and the second	-1	2	Cu*/ Cu ²⁺	N/A	2.6
12	Cu ₂ (BTC) ₂ (OH)		0	2	Cu*/ Cu ²⁺	N/A	1.4
13	Cu2(BTC)3 (OH)_mu2		0	3	Cu ²⁺ / Cu ²⁺	0.0	0.1
14	Cu2(BTC)3 (OH)_mu1			3	Cu ²⁺ / Cu ²⁺	+0.3	1.2

15				1	Cu*/ Cu ³⁺	+0.8	4.2
16	Cu ₂ (BTC) ₃		0	2	Cu*/ Cu ²⁺	N/A	0.6
17	Cu ₂ (BTC) ₃	Je Contraction	0	2	Cu*/ Cu²+	0.0	1.6
18	- (H ₂ O)		U	2	Cu+/ Cu ²⁺	+0.02	3.7



^a Overall charge of the molecular complex; ^b Multiplicity (*M* = 2*S* + 1) of the molecular complex; ^c Relative bonding energy indicating the relative stability of the complexes. Applicable for complexes of the same type with different multiplicity (**4** and **5**, **6** and **7**, **8** and **9**, **14** and **15**), and for complexes that are structural isomers (**13** and **14**, **17** and **18**); ^d Calculated energy difference between the 2p electronic states of the copper ions in the respective metal-metal pairs; ^e Structures derived after constrained geometry optimizations with fixed terminal carboxylate oxygens (from the COOH groups of the molecular model).

Supporting Information 6: SURMOF mass change during immersion in liquid ethanol



Figure SI6: The mass change of the SURMOF during the immersion in liquid ethanol at 65°C. The mass change is determined from the change of the absolute values of the resonance frequency und using the Sauerbrey equation. The data are from the first two cycles of Figures 2c and SI2. 2 samples were investigated simultaneously. The resonance frequencies were determined of the activated (empty) SURMOFs before the cyclohexane uptake started.

The initial SURMOF mass was 8.8 μ g cm⁻² (black) and 9.9 μ g cm⁻² (red). As a result, the mass of the SURMOF decreased by roughly 20%.

Supporting Information 7: Infrared spectra of HKUST-1 MOF exposed to D₂O



Figure SI7: IRRA spectra of the pristine SURMOF (black), after 3 h exposure to heavy water D_2O (blue). A small band of adsorbed OD, according to ref.^[9], can be seen, indicating that the water molecules dissociate when forming the defect structure.

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