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Herein, we report on the synthesis of highly oriented and nanostructured metal-organic framework (MOF) films featuring extreme surface wetting properties. The Ni- and Co- derivatives of the metal-catecholate series (M-CAT-1) were synthesized as highly crystalline bulk materials and thin films. Oriented pillar-like nanostructured M-CAT-1 films exhibiting pronounced needlelike morphology on gold substrates were established by incorporating a crystallization promoter into the film synthesis. These nanostructured M-CAT-1 MOF films feature extreme wetting phenomena, specifically superhydrophilic and underwater superoleophobic properties with water and underwater oil-contact angles of 0° and up to 174°, respectively. Self-cleaning capabilities for the nanostructured, needle-like M-CAT-1 films were illustrated by measuring time-dependent oil droplet rolling-off a tilted surface. The deposition of the nanostructured Ni-CAT-1 on large glass substrates allowed for the realization of an efficient transparent anti-fog coating enabling a clear view even at extreme temperature gaps up to ca. 120 °C. This work illustrates the strong link between MOF film morphology and induced surface properties based on these framework materials.

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Nanostructured and Oriented Metal-Organic Framework Films enabling Extreme Surface Wetting Properties

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**ABSTRACT:** Herein, we report on the synthesis of highly oriented and nanostructured metal-organic framework (MOF) films featuring extreme surface wetting properties. The Ni- and Co- derivatives of the metal-catecholate series (M-CAT-1) were synthesized as highly crystalline bulk materials and thin films. Oriented pillar-like nanostructured M-CAT-1 films exhibiting pronounced needle-like morphology on gold substrates were established by incorporating a crystallization promoter into the film synthesis. These nanostructured M-CAT-1 MOF films feature extreme wetting phenomena, specifically superhydrophilic and underwater superoleophobic properties with water and underwater oil-contact angles of 0º and up to 174º, respectively. Self-cleaning capabilities for the nanostructured, needle-like M-CAT-1 films were illustrated by measuring time-dependent oil droplet rolling-off a tilted surface. The deposition of the nanostructured Ni-CAT-1 on large glass substrates allowed for the realization of an efficient transparent anti-fog coating enabling a clear view even at extreme temperature gaps up to ca. 120 ºC. This work illustrates the strong link between MOF film morphology and induced surface properties based on these framework materials.

Over millions of years plants and animals have evolved a spectrum of surface designs enabling specific wetting properties tailored for their survival in extreme conditions. In plants, the unique surface architecture of the lotus leaf enables superhydrophobic and self-cleaning properties for sustaining efficient photosynthesis even in polluted environments. In the realm of animals, mosquitoes utilize an anti-fog coating covering their eyes for a clear vision in high humidity regions. The fogstand beetles employ an anti-fog coating for enhancing water vapor harvesting abilities in dry climates. In marine life, fish protect themselves from oil-polluted environments or avoid biofouling due to oil-repellent designs and self-cleaning capabilities of their skin. These intriguing super-hydrophilic or -oleophobic surface characteristics are obtained by the combination of precise chemical compositions and hierarchical microstructuring of the surface. Nowadays, modern surface technologies such as anti-fog or -fouling, oil-repelling coatings, self-cleaning surfaces and water-harvesting systems are inspired by nature’s designs. The synthesis of artificial super-hydrophilic surfaces can be achieved by a variety of routes, e.g., sol-gel synthesis, electrochemical deposition, anodization, electrochemical polymerization, electrospinning, plasma treatment, chemical or hydrothermal methods, vapor-deposition, layer-by-layer assembly or laser ablation. However, the development of a straight-forward and versatile bottom-up synthesis scheme enabling tunable surface morphologies for controlled wetting properties is still challenging and highly desired.

Metal-organic frameworks (MOFs) are crystalline and porous materials featuring a great structural and chemical diversity. Thereby, they are attractive synthesis targets for a large variety of applications including gas storage and separation, chemical sensing, thermoelectrics, capacitors, transistors or photovoltaics. However, only a few reports describe MOFs featuring superhydrophilic, superhydrophobic, superoleophilic or superoleophobic properties. Typically, desired wetting properties in MOFs were mostly chemically induced by post-synthesis modification or by including building blocks decorated with hydrocarbon side chains. Very recently, a copper mesh decorated with hybrid Cu(OH)2/ MOF nanobrushes showed wetting properties with contact angles suggesting superoleophobic properties. Therefore, the use of well-defined thin MOF films as target architectures for encoding on-surface wetting properties is yet to be revealed.

Here, we present the synthesis of highly oriented and nanostructured MOF films mimicking architectures observed in nature, resulting in highly unusual, extreme surface wetting properties. For the synthesis, the Ni- and Co- derivatives of the metal-catecholate series (M-CAT-1) were selected. First, these M-CAT-1 derivatives were synthesized as highly crystalline bulk materials. The M-CAT-1 surface energies were estimated by contact angle measurements using pellet samples exposing randomly distributed crystallites on the surface. Next, oriented and compact Co- and Ni-CAT-1 films were deposited on gold surfaces by vapor assisted-conversion (VAC). These films showed enhanced hydrophilic and underwater oleophobic properties compared to the corresponding pressed pellet samples.
Oriented, nanostructured M\textsuperscript{-CAT-1} films exhibiting pronounced needle-like morphology on gold substrates were obtained by adding a crystallization promoter into the VAC precursor solution. These nanostructured M\textsuperscript{-CAT-1} MOF films feature extreme wetting phenomena, specifically superhydrophilic and underwater superoleophobic properties with water and underwater oil-contact angles of 0\(^\circ\) and up to 174\(^\circ\), respectively. Self-cleaning capabilities for the nanostructured, needle-like Ni and Co\textsuperscript{-CAT-1} films were illustrated by measuring time dependent oil droplet rolling-off a tilted surface. The deposition of the nanostructured Ni\textsuperscript{-CAT-1} on large glass substrates allowed for the realization of an efficient anti-fog coating based on the M\textsuperscript{-CAT-1}. These anti-fog coatings enabled clear vision even at extreme temperature differences of up to 120\(^\circ\) C.

RESULTS AND DISCUSSION

The M\textsuperscript{-CAT-1} MOFs are crystalline microporous structures obtained by a solvothermal reaction of metal precursors and the organic building block 2,3,6,7,10,11-hexahydroxytriphenylene (HHTP) as a dark precipitate. The M\textsuperscript{-CAT-1} crystallites exhibit hexagonally faceted needle-like morphology with typical crystal cross-sections of 30-40 nm and several \(\mu\)m in length (Figure 1). In addition, M\textsuperscript{-CAT-1} materials are electroactive featuring electrical conductivity values of up to \(10^{-2}-10^{-3}\) S cm\(^{-1}\) for pressed powder pellets and oriented thin films, respectively. However, the wetting properties of these MOFs both as pristine powders and as films have not been explored.

For our study, we focused on the Ni- and the Co\textsuperscript{-CAT-1}, since their structure is well-characterized and elucidated by diffraction methods, serving as a good basis for understanding their growth behavior and morphology. To assess the wetting properties of Ni- and Co\textsuperscript{-CAT-1}, we investigated the interaction of bulk materials pressed as compact pellets with different polar and apolar liquids. For this purpose, we synthesized M\textsuperscript{-CAT-1} bulk materials following our recently published solvothermal
Synthesis procedure (more details see Figure S.3.1). Subsequently, the obtained MOF powders were collected, activated under dynamic vacuum and pressed into crystalline pellet samples (1 cm diameter, thickness 500 µm; 100 mg activated MOF, roughness (RMS): 37 nm). Scanning electron microscope (SEM) micrographs reveal densely packed and randomly distributed MOF crystallites throughout the sample (see Figure S3.2). For the contact angle (CA) measurements at the solid/air interface we chose diiodomethane as a non-polar organic liquid exhibiting relatively high surface tension and water as a polar liquid (see Figure 1). Diiodomethane contact angle measurements on the M-CAT-1 pellets reveal shallow angles of about 12° whereas water revealed values of about 46°. This illustrates that in air the M-CAT-1 materials feature an amphiphilic character, namely hydrophilic and superoleophilic properties. This amphiphilic wetting property can be attributed to a high surface energy of the MOF materials. To estimate the corresponding MOF surface energies, we applied Fowker’s theory, where the observed contact angle between a liquid and a solid is the sum of a polar and a dispersive component of the liquid’s surface tension. Utilizing the measured contact angles of diiodomethane exhibiting solely a dispersive component and water, having a dispersive and a polar component, enabled the calculation of the overall surface energy for Ni- and Co-CAT-1. (for detailed discussion see SI, table 1). We obtained surface energies of 64.02 and 62.38 mN/m for the Ni- and Co-CAT-1 pellet samples, respectively. These values are higher than the surface energies reported for oleophilic polymers featuring surface energies in the range of 20-50 mN/m. However, the estimated MOF surface energies are in good agreement with systems such as modified carbonaceous layers, showing values of about 60 mN/m and water contact angles (WCA) of 50°, which agrees well with the obtained water contact angles on the M-CAT-1 pellets. Superoleophilic wetting properties were also detected for chlorinated oils such as dichloromethane on M-CAT-1 pellets (see Figure S3.4). This further illustrates the amphiphilic nature of M-CATs, showing hydrophilic as well as superoleo-

Figure 2. A) Synthesis scheme of the vapor-assisted conversion set up and the resulting nanostructured films. B) SEM top-view, 30° tilted cross-section and the related GIWAXS pattern of Co-CAT-1. C) SEM top-view, 30° tilted cross-section and the related GIWAXS pattern of Ni-CAT-1.
philic behavior towards several different oils. Interestingly, underwater oil contact angles (OCA) of diiodomethane on these pellets reveal an inverse wetting phenomenon. Under these conditions, the M-CAT-1 materials reject oil and turn oleophobic with OCA of 90° (Figure 1I).

Table 1. Overall surface energies ($\sigma_s$) and the respective dispersive ($\sigma_s^D$) and polar ($\sigma_s^P$) components estimated for Ni- and Co-CAT-1 pellet samples.

| M-CAT-1 | $\sigma_s$ [mN/m] | $\sigma_s^D$ [mN/m] | $\sigma_s^P$ [mN/m] |
|---------|-----------------|-----------------|-----------------|
| Ni-CAT-1 | 64.02           | 49.69           | 14.06           |
| Co-CAT-1 | 62.38           | 50.30           | 12.08           |

Constructing nanostructured M-CAT-1 surfaces. According to Wenzel’s model, film topography has a strong impact on the wetting properties of a surface. Following this line of thought, we aimed at constructing M-CAT-1 thin films featuring distinct surface morphologies, hence allowing for achieving desired surface wetting properties. However, on-surface control of MOF film morphology is a challenging task due to the specific growth conditions required for maintaining key features such as homogeneity, crystallinity and crystal orientation on the surface. In our previous reports, we have demonstrated that the use of a modulator in combination with the choice of a substrate can play a crucial role in VAC synthesis for the formation of a crystalline MOF film. In the present study, we introduce the use of a crystallization promoter in the VAC process, solely for inducing distinct film morphology while maintaining crystallinity and the crystal orientation on a preselected substrate.

Accordingly, we employed VAC methods for producing both compact and nanostructured M-CAT-1 films (see Figure S5.1). Briefly, thin and oriented films of Ni- and Co-CAT-1 were synthesized on gold substrates by depositing a thin layer of a precursor solution onto a gold substrate. Then, the gold substrate was placed on a glass platform above a solvent bath inside a glass autoclave. Subsequently, the reactor was sealed and placed for 12 hours at 85°C in a preheated oven. After 12 h reaction time, the reactor was removed from the oven and allowed to cool down to room temperature. The substrates were recovered, washed and dried under N$_2$ stream revealing a colored film on the gold substrate. These films typically exhibit 150 nm thickness, consisting of highly intergrown oriented crystallites (see Figure S5.1).

Next, nanostructured pillar-like M-CAT-1 films were synthesized by employing carboxylic acids serving as crystallization promoters in the drop-cast precursor solution layer. Specifically, we introduced acetic acid in the Ni-CAT-1 and salicylic acid in the Co-CAT-1 synthesis (see Figure 2A). Top-view
scanning electron microscopy (SEM) images show a homogenous film and a long-range ordered array of pillar-like structures with 20-30 nm pillar cross-section and evident gaps between pillars of about 150 nm for both samples (see Figure 2B and 2C).

Cross-section SEM micrographs clearly visualize an array of vertical MOF needles on the surface plane. In addition, a uniform film thickness of about 800 nm is observed throughout the cross-section of both Ni- and Co-CAT-1 samples, indicating a self-terminating growth under the conditions employed (Figure 3B, Figure S5.2). To confirm that besides defining a nanostructured textured surface, the needles are indeed crystalline and well-aligned orthogonally to the surface plane, X-ray grazing incidence wide angle scattering (GIWAXS) experiments were performed (see Figure 2B, 2C). The GIWAXS patterns indicate the formation of crystalline M-CAT-1 structures, and the observed reflections were indexed according to the corresponding reported M-CAT-1 PXRD patterns (for further information see SI). Distinct reflections at \(q_x = 3.9 \text{ nm}^{-1}\) (100), \(q_y = 7.1\ \text{nm}^{-1}\) (200) and \(q_z = 9.2\ \text{nm}^{-1}\) (210) near \(q = 0\ \text{nm}^{-1}\), referred to as out-of-plane reflections, indicate the preferential orientation of the crystallites where the crystal c-axes are aligned orthogonally to the surface. The (004) reflection corresponding to an interlayer distance of 3.3 Å is observed as a diffuse arc at around \(q = 19\ \text{nm}^{-1}\), also pointing towards a preferential crystal orientation. These data show that by employing the VAC synthesis in the presence of a crystallization promoter, the fabrication of crystalline highly nanostructured and oriented M-CAT-1 films on gold substrates is feasible.

Superhydrophilic and underwater superoleophobic MOF-based surfaces. Following Wenzels’ equation, \(^{70}\) increased surface roughness results in a decreased WCA and in an enhanced underwater OCA. To study the impact of roughness on the wetting properties of the M-CAT-1 films, we performed WCA and underwater OCA measurements for the compact and the nanostructured M-CAT-1 films (see Figure 3, S5.3).

Oriented compact films reveal CAs of 32° and 26° for Ni- and Co-CAT-1, respectively, whereas oriented pillar-like nanostructured films feature a drastic decrease in WCAs (see Figure S5.3, S5.5). Strikingly, we observed complete water spreading on the M-CAT-1 films and a WCA of 0° for both films, thus rendering these surfaces superhydrophilic (Figure 3C, 3D). These observed surface properties were further confirmed by measuring the underwater OCA with a droplet of dichloromethane (DCM). Thereby, oriented compact films showed enhanced oleophobic properties with underwater OCAs of about 130° and 133° for Ni- and Co-CAT-1, respectively (see Figure 3, S5.3). Remarkably, for oriented pillar-like nanostructured films, we observed a strong increase of the OCAs and extreme values of 174° and 173° were determined for Ni- and the Co-CAT-1, respectively (see Figure S5.3). On these films, a nearly perfect oil sphere is formed, which hardly comes in contact with the surface (see Figure 5). These surface properties resemble those of surface designs found in nature. For example, referring to marine life, fish scales in air show an amphiphilic behavior due to their high surface energy, but under water they turn superoleophobic, which is of great advantage for protection against hazardous environments, e.g., oil-polluted water.

The self-cleaning properties of these extremely oleophobic M-CAT-1 nanostructured surfaces were demonstrated by casting a DCM oil droplet on a marginally tilted substrate (e.g., by 1.4°). Subsequently, the motion of the droplet was recorded by a high-speed camera with 3 fps (see Figure 3G and S5.4). The obtained image series reveals that a droplet crosses the substrate and rolls out of the detection range of the high-speed camera in about 1.3 s. According to the Cassi-Baxter theory, the very low tilt-angle required for the droplet rolling off the substrate combined with the extreme underwater OCA angles suggests that the DCM sphere comes in contact only with the tips of the crystalline needles whereas the intercrystallite areas are interacting solely with water (Figure S7.1).72 To exclude the contribution of the gold surface to wetting properties of the MOF films we carried out control experiments with blank gold substrates giving WCA of 94° and underwater OCA of 52° (see Figure S4.1). This confirms that the observed superhydrophilic and superoleophobic behavior arises from the MOF film and not from the substrate.

To establish these MOF films as superoleophobic surfaces applicable to a wide range of oils, we examined the interactions of other high-density liquids with the oriented and nanostructured MOF surfaces. For this purpose, we determined the underwater OCAs for different chlorinated liquids such as dichloromethane (DCM), dichloroethane (DCE), chloroform (CHCl3) and chlorobenzene (PhCl). The OCAs were recorded using the exact same procedure described for DCM and the results are plotted as box-and whisker plots in Figure 4. For all the measured oils, superoleophobic behavior was observed with extreme OCAs ranging from 155° (DCE) for Co-CAT-1 to 169° (PhCl) for Ni-CAT-1 films. Specifically, Ni-CAT-1 exhibits the following OCAs: 174° (DCM), 162° (DCE), 165° (CHCl3) and 169° (PhCl), whereas Co-CAT-1 exhibits 173° (DCM), 158° (DCE), 155° (CHCl3) and 162° (PhCl). These results confirm...
that the MOF films efficiently repel a large variety of oily liquids, hence constituting an intriguing platform for designing underwater superoleophobic properties.

Since MOFs are crystalline materials featuring different crystal facets having distinct surface energies, the orientation of these crystallites on a surface is expected to impact the wetting properties. In the following we discuss the case of Ni-CAT-1 as a model for the M-CAT-1 series. In the context of crystal orientation on the surface, we analyzed the Ni-CAT-1 WCA of pressed pellet samples and those of oriented and compact films. Interestingly, pressed pellets consisting of randomly distributed crystallites on the surface exhibit greater WCAs than oriented films although showing slightly increased surface roughness (see Figures S3.5, S3.6, S5.2, S5.3). We attribute this difference to the different surface character which directly impact the surface energies hence the wetting properties (see table S1). We therefore conclude that the observed wetting properties are a combination of two different significant contributions which can be controlled by the VAC process, namely the surface roughness and the crystallite orientation on the substrate.

Figure 5. A) 30° tilted SEM top-view SEM image of Ni-CAT-1 grown on glass by using a crystallization additive in the VAC synthesis. B) WCA of the superhydrophilic nanostructured Ni-CAT-1 surface. C) Macroscopic image of the Ni-CAT-1 sample showing the complete spread of the water droplet. D) Anti-fog coating experiment performed with a bare glass slide placed above a glass vessel containing a reservoir of hot water at boiling temperature. E) The LMU seal obscured by water droplet condensation on the bare glass. F) Anti-fog coating experiment performed with a MOF-coated glass above a glass vessel containing a reservoir of hot water at boiling temperature. G) High transparency and visibility through the substrate and a visible LMU seal.
Anti-fog coating by MOFs. Water condensation on surfaces is a known phenomenon occurring at the dew point on substrates such as glass serving as favorable nucleation sites for water droplets. This process leads to a substantial reduction in the glass's transparency and the vision through the glass becomes extremely limited. To avoid condensation, modifications of the glass surface with different classes of functional coatings are necessary. Motivated by the superhydrophilic properties obtained by growing nanostructured M-CAT-1 films on gold substrates, we investigated the synthesis of such films as transparent coatings on glass substrates, thereby modifying their wetting character towards superhydrophilic properties. Through this approach, a thin water layer decorating the textured MOF surface is expected to form, hindering the nucleation of water droplets on the glass surface. For this purpose, we employed the newly developed methodology for the synthesis of nanostructured Ni-CAT-1 films on gold substrates with a slightly modified synthesis procedure addressing larger substrate dimensions such as 2.5 cm x 2.5 cm. The resulting MOF films on glass substrates reveal a slightly blue yet transparent coating (see Figure 5C, 5F). A top-view SEM micrograph revealed the typical orthogonally aligned needle-like nanostructures on the surface similar to the M-CAT-1 films grown on gold surfaces. The preferential orientation of the MOF crystals on the glass substrate was further confirmed by GIWAXS measurements (see Figure S5.6). The WCA measurements showed superhydrophilic properties similar to those observed for gold substrates (Figure 5C). Further conducted control experiments confirmed that the superhydrophilic wetting properties originate from the nanostructured MOF film. Blank glass substrates give WCA of 11° and OCA of 81° (see Figure 4.2). Furthermore, the MOF films endow the glass substrates with light-absorbing properties while maintaining transparency (see Figure S5.8).

To test the anti-fog coating properties of the Ni-CAT-1 MOF film, a glass vessel containing a reservoir of boiling water (ca. 100 °C) was placed above an LMU seal, and a non-modified glass substrate was positioned on top of the open vessel (see Figure 5D, F, S6.1). In seconds, the seal was no longer visible, obscured by the water droplets generated by the condensation of steam on the glass surface (Figure 5E). In contrast, using a MOF-coated glass substrate, high transparency and clear visibility through the substrate was enabled and the seal was visible even after longer exposure times (Figure 5F, 5G). To examine the behavior of the anti-fog coating in extreme temperature differences, the MOF-modified glass substrates were cooled down to -20°C and subsequently placed on top of the hot water reservoir. Under all examined conditions, a clear vision through the glass was maintained and water vapor nucleation was not observed (see Figure S6.2). This striking effect is attributed to the formation of a thin water layer on the MOF films which spreads out completely on the surface. This thin water layer is clearly visible by turning the substrate upside down (Figure 5G). This set of experiments establishes the pillar-like nanostructured Ni-CAT-1 films as highly efficient anti-fog coatings featuring additional desired properties such as light absorbance. Furthermore, it underlines the power of VAC enabling the synthetic bottom-up fabrication of MOF films with well-defined nanoscale morphologies and associated functionality.

CONCLUSION

In this study, we demonstrated the controlled on-surface synthesis of crystalline, highly oriented and nanostructured M-CAT-1 films by using a crystallization promoter in the VAC synthesis. First, the free surface energy of M-CAT-1 was calculated for pressed pellet samples shedding light on the amphiphilic wetting properties of the material in air, being both hydrophilic and oleophilic. Oriented and compact M-CAT-1 films exhibit enhanced wetting properties were shallower contact angles were determined for water (about 32°) and large underwater OCA (130°) indicating oleophobic properties. The corresponding oriented pillar-like nanostructured M-CAT-1 films exhibit extreme wetting properties with WCA of 0° and underwater OCAs of 174°, being superhydrophilic and superoleophobic in water.

The underwater self-cleaning abilities of these films were demonstrated by depositing an oil droplet on a substrate tilted at a shallow angle of 1.4°. The effective underwater oil-repelling properties of the M-CAT-1 films were confirmed with a range of different chlorinated oily liquids. Under ambient atmosphere, the water wetting properties of these systems could be drastically altered by changing the film morphology from compact to pillar-like nanostructured. This effect was also transferred onto transparent substrates such as glass, resulting in an efficient transparent MOF-based anti-fog coating. Hence, we demonstrate that on-surface alteration of MOF film morphology by versatile solution-based bottom-up methods such as VAC is a powerful tool for realizing the potential of MOFs in surface-based technologies such as oil-water separation systems, anti-oil coatings, or self-cleaning surfaces.

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ABBREVIATIONS

WCA, water-contact angle; OCA, oil-contact angle; VAC, vapor-assisted conversion; MOF, metal-organic framework; M CAT-1, metal-catecholates.

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Supporting Information

Nanostructured and Oriented Metal-Organic Framework Films enabling Extreme Surface Wetting Properties

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1. Characterization

**X-ray spectroscopy**

X-ray diffraction (XRD) analyses were performed on a *Bruker D8* diffractometer in Bragg-Brentano geometry with Ni-filtered Cu $K_\alpha$ ($\lambda = 1.54060$ Å) radiation operating at 40 kV and 30 mA with a position-sensitive detector (*LynxEye*).

Two-dimensional grazing-incident wide angle X-ray scattering (2D GIWAXS) data were collected using an *Anton-Paar SAXSpace system* equipped with a Cu $K_\alpha$ microfocus source operated at 50 kV and 1 mA and an *Eiger Dectris R 1M* 2D detector.

**Scanning electron microscopy (SEM)**

SEM images were recorded on a *FEI Helios NanoLab G3 UC* electron microscope with an acceleration voltage of 2 kV from a field emission gun. For the cross-section analysis substrates were partially cut and broken manually to reveal fresh cross-sections. Prior to SEM analysis the samples were coated with a thin carbon layer by carbon fiber flash evaporation in high vacuum.

**Transmission electron microscopy (TEM)**

TEM images were collected on a *FEI Titan Themis 60-300* microscope at an acceleration voltage of 300 keV. Powder samples were prepared by crushing the particles with a razor blade and subsequently depositing the powder onto a copper grid supporting a thin electron transparent carbon film. TEM film samples were prepared by carefully removing the film layer on top of the substrate with a sharp blade and mounting it onto the sample grid.

**Nitrogen sorption**

Ad- and desorption measurements were performed on an Autosorb 1 (*Quantachrome instruments, Florida, USA*) with nitrogen of 99.9999% purity at 77.3 K. The samples were activated under high vacuum at 120 °C for at least 12 h. Evaluation of ad- and desorption isotherms was carried out with the program *AsiQwin v.3.01* (*Quantachrome instruments, Florida, USA*).

For BET calculations, pressure ranges of the nitrogen isotherms were chosen with the help of the BET assistant in the *AsiQwin software*. In accordance with the ISO recommendations, multipoint BET tags equal to or below the maximum in $V \times (1-p/p_0)$ were chosen.
Contact angle measurements

Contact-angle measurements were performed on an atension from Biolin Scientific. A droplet with the sessile drop method. A droplet of liquid was placed on the substrate, while recording images with 1 fps for 10s, while the dynamic measurements (self-cleaning surfaces) were recorded with 3 fps for 10 s. The image analysis was carried out with the software ImageJ using the manual mode and fitting the contour of the droplets manually.

Atomic force microscopy (AFM)

AFM measurements were performed using a NANOINK atomic force microscope in tapping mode with a scanning rate of 0.2 Hz, a proportional gain of 50 and an integral gain of 32. The scanned area was 5.02 × 5.02 µm at 282 × 282 pixels.

2. Experimental

General

All materials were purchased from Sigma Aldrich, Acros or TCI Europe in the common purities purum, puriss or reagent grade. The materials were used as received without additional purification and handled in air unless otherwise noted. The water utilized in the synthesis was subjected to a Merck-Milipore Mili-Q purification system prior to use.

Substrates

The preparation of the gold substrates was based on the procedure described by Hinterholzinger et al. Seven microscope glass slides (Menzel, 76 mm x 26 mm) in a support made of Teflon were cleaned by ultrasonic treatment in acetone, followed by sequential washing steps with 2-propanol, a 1:100 mixture of Hellmanex III and water, and finally 2-propanol (Chromasolv). Oxygen plasma cleaning (Diener electronic, Plasma-Surface-Technology) for 30 min was conducted, previous to the mounting of the glass slides in a vacuum deposition unit installed in a glove box (MBraun Labmaster Pro SP equipped with an Inficon SQC-310C Deposition controller). 10 nm of titanium and 40 nm of gold were thermally deposited under high vacuum onto the microscope glass slides.
The respective substrates were prepared by cutting commercially available microscope slides (Menzel, 76 mm x 26 mm), gold coated glass slides into pieces of 1.2 cm x 1.0 cm and 2.5 cm x 2.5 cm.

**Bulk Synthesis**

**Ni-CAT-1**

In a 5 mL culture tube, a solid mixture of 2,3,6,7,10,11-hexahydroxytriphenylene (0.0107 mmol, 3.5 mg) and nickel(II) acetate tetrahydrate (0.0201 mmol, 5 mg) was suspended in 1 mL 1-propanol and 1 mL distilled water (1:1 v:v). The loading of the culture tube was carried out under ambient atmosphere and the resulting blue solution was sonicated for 10 s at maximum power. Subsequently, the culture tube was tightly capped and heated at 85 °C for 18 h in a preheated oven. The resulting black solution was washed three times with 10 mL dry acetone and isolated by centrifugation. The obtained dark blue microcrystalline product was dried under dynamic vacuum prior to analysis.

**Co-CAT-1**

In a 5 mL culture tube, a solid mixture of 2,3,6,7,10,11-hexahydroxytriphenylene (0.0107 mmol, 3.5 mg) and cobalt(II) acetate tetrahydrate (0.0207 mmol, 5 mg) was suspended in 1 mL of 1-propanol and 1 mL of distilled water (1:1 v:v). The loading of the culture tube was carried out under ambient atmosphere and the resulting blue solution was sonicated for 10 s at maximum power. Subsequently, the culture tube was tightly capped and heated at 85 °C for 18 h in a preheated oven. The resulting black solution was washed three times with 10 mL of dry acetone and isolated by centrifugation. The obtained dark blue microcrystalline product was dried under dynamic vacuum prior to analysis.

**Preparation of Ni- and Co-CAT-1 pellets**

Ni- (110.5 mg) and Co- (95.8 mg) CAT-1 pellets (obtained from several of the above described batches) for electrical conductivity measurements were fabricated with a standard Paul-Weber KBr Press.

**Film formation via vapor-assisted conversion (VAC)**

For the film formation using VAC, a glass bottle (Schott Duran, borosilicate 3.3, ISO4796, 100 mL) with a PBT cap equipped with a Teflon seal was used. The bottom part of the bottle was
filled with 14 Raschig-rings (10 mm x 10 mm, soda-lime glass) to obtain an elevated flat platform for the substrate. A mixture of water and 1-propanol was filled into the bottle. Afterwards, a substrate (1.2 cm x 1 cm) was placed on top of the Raschig-rings and fully coated with a liquid layer of a freshly prepared MOF precursor solution. The bottle was closed and transferred into a preheated oven where it was kept for the specified time. Afterwards, the autoclave was removed from the oven and cooled down for 10 min before the substrate was rinsed with dry acetone.

**Synthesis of compact Ni- and Co-CAT-1 films on gold surfaces**

The HHTP precursor (2.69 x 10^{-3} mmol; 0.875 mg) and the metal precursors nickel acetate (5.0 x 10^{-3} mmol; 1.25 mg), cobalt acetate (5.0 x 10^{-3} mmol; 1.25 mg) or copper trifluoroacetylacetone (5.0 x 10^{-3} mmol; 1.25 mg) were mixed in a defined ratio (1:2) and dissolved in a solvent mixture of water and 1-propanol (1.5 mL: 1.5 mL) by sonication for 20 s at maximum power. The obtained precursor solution was filtered through a syringe filter to remove any remaining particles. Subsequent, 40 µL of the solution (HHTP: 0.899 mmol L^{-1}; MOAc: 1.674 mmol L^{-1}) were deposited onto a clean 1.2 x 1.0 cm gold substrate. Four of these set-ups were placed onto glass spacers in an autoclave loaded with a solvent mixture of water and 1-propanol (2.5 mL: 2.5 mL). The autoclave was sealed immediately and placed into a preheated oven at 85 °C for 3.5 h. The experimental set-up of the VAC is shown in Fig. S2.1. Afterwards, the autoclave was removed from the oven and cooled down for 10 min before the substrate was rinsed with dry acetone.
Synthesis of nanostructured Ni-CAT-1 films on gold substrates

The precursor solution was prepared by providing a hexahydroxytriphenylene (HHTP) precursor (5.4 x 10^{-3} mmol; 1.75 mg) as organic building blocks and nickel acetate (10 x 10^{-3} mmol; 2.5 mg) as metallic precursors in a defined ratio (1:2 n:n) and dissolving them in a solvent mixture of water and 1-propanol (1 mL : 1 mL) with the addition of the modulator acetic acid (50 μL). 40 μL of the respective precursor solution (HHTP: 5.35 mmol L^{-1}; NiAc: 10.7 mmol L^{-1}; HOAc: 1.745 mol L^{-1}) was dropcasted onto the main surface of a clean 1.2 x 1.0 cm glass substrate having a gold-coated main surface. Four of such substrates, each carrying a droplet of precursor solution, were placed onto glass spacers as substrate holders in an autoclave partly filled with a solvent bath consisting of water and 1-propanol (2.5 mL : 2.5 mL). The autoclave was sealed immediately and placed into a preheated oven at 85°C for 18 hours. Afterwards, the autoclave was removed from the oven and cooled down for 10 min, before the substrates were rinsed off with dry acetone.

Synthesis of nanostructured Co-CAT-1 films on gold substrates

The precursor solution was prepared by providing an HHTP precursor (5.4 x 10^{-3} mmol; 1.75 mg) as organic building blocks and Cobalt acetate (11.0 x 10^{-3} mmol; 3 mg) as metallic precursors in a defined ratio (1:2.5 n:n) and dissolving in a solvent mixture of water, 1-propanol (1 mL : 1 mL) with addition of 50 μL of a water, 1-propanol solution (1 mL : 1 mL) containing salicylic acid as a modulator (0.89 mmol; 125 mg). 40 μL of the respective precursor solution (HHTP:5.35 mmol L^{-1}; CoAc: 12.85 mmol L^{-1}; salicylic acid: 11.23 mmol L^{-2}) was dropcasted onto a clean 1.2 x 1.0 cm substrate. Four of such substrates, each carrying a droplet of precursor solution, were placed onto glass spacers as substrate holders in an autoclave partly filled with a solvent bath consisting of water and 1-propanol (2.5 mL : 2.5 mL). The autoclave was sealed immediately and placed into a preheated oven at 85°C for 18 h. Afterwards, the autoclave was removed from the oven and cooled down for 10 min, before the substrates were rinsed off with dry acetone.

Synthesis of nanostructured Ni-CAT-1 films on glass substrates

The HHTP precursor (5.4 x 10^{-3} mmol; 1.75 mg) and the nickel acetate (10.0 x 10^{-3} mmol; 2.5 mg) were mixed in a defined ratio (1:2) and dissolved in a solvent mixture of water and 1-propanol (1 mL : 1 mL) with the addition of the modulator acetic acid (50 μL). 100 μL of the
respective precursor solution (HHTP: 5.35 mmol L\(^{-1}\); NiAc: 10.7 mmol L\(^{-1}\); HOAc: 1.745 mol L\(^{-3}\)) were deposited onto a clean 2.5 x 2.5 cm glass substrate. One of this set-ups was placed onto glass spacers in an autoclave loaded with a solvent mixture of water and 1-propanol (2.5 mL : 2.5 mL). The autoclave was sealed immediately and placed into a preheated oven at 85 °C for 18 h. Afterwards, the autoclave was removed from the oven and cooled down for 10 min before the substrates were rinsed with dry acetone.
3. Characterization of the M-CAT-1 bulk material

PXRD and SEM analysis of Ni- and Co-CAT-1 bulk materials

Figure S3.1 A) PXRD pattern of the Ni- and Co-CAT-1 (red and blue) bulk materials compared to the calculated Co-CAT-1 pattern. B) and C) show the needle-like bulk morphology of the Ni- and Co-CAT-1 samples, respectively.

PXRD and SEM analysis of pelletized Ni- and Co-CAT-1 samples

Figure S3.2 A) PXRD pattern of the Ni- and Co-CAT-1 (red and blue) pelletized materials compared to the calculated Co-CAT-1 pattern. B) and C) show the dense needle-like bulk surface of the Ni- and Co-CAT-1 pelletized samples, respectively.
Water and Oil-contact angles of Ni- and Co-CAT-1 pellets in water

Figure S3.4 A) and B) Water-contact-angle of Ni- and Co-CAT-1 pellet samples in air, respectively. C) and D) underwater dichloromethane -contact angle of Ni- and Co-CAT-1 pellet samples, respectively.

Atomic force microscopy (AFM) image of M-CAT-1 Pellets

Figure S3.5 AFM topographic measurement of a 4.5 um x 4.7 um area from a Ni-CAT-1 pelletized sample. The surface roughness values were calculated to be and 37 (Rms) nm.
Surface energy of M-CATs

The wetting properties of the M-CAT-1 bulk material were estimated by the following procedure. First, M-CAT-1 bulk material were prepared according to a literature procedure and pelletized the obtained microcrystalline powder to pelletized samples (1 cm diameter, thicknesses 500 μm; 100 mg material). The samples exhibit an even surface composed of densely packed and randomly oriented crystallites, this was confirmed by scanning-electron microscopy (SEM) and X-ray diffraction (XRD) analysis and atomic force microscopy (AFM). On the as-prepared pelletized samples we performed contact angle (CA) measurements to estimate first, the free solid surface energy of the material, especially the dispersive and polar components. Free surface energy of a solid cannot be directly measured, but it can be calculated from a set of steady state liquid/solid contact angles. Therefore, we used the most common method for estimating the free surface energy, the Fowkes theory. This theory describes surface energy of a solid as composed of a dispersive component, and “non”-dispersive part (polar). It is therefore based on the Young’s equation and the Dupre’s definition of adhesion energy showing that the adhesive energy between a solid and a liquid can be separated into dispersive interactions and the non-dispersive (polar) interactions between two phases.

These two energy expressions \( \text{e.g. Young’s} \) and the \( \text{Dupre’s} \) equations can be combined to yield the Fowkes’ surface energy equation:
\[(\sigma_L^D)^{1/2}(\sigma_S^D)^{1/2} + (\sigma_L^P)^{1/2}(\sigma_S^P)^{1/2} = \frac{\sigma_L(\cos\theta + 1)}{2}\]  

(1)

With \(\sigma_L^D\) = surface tension liquid (dispersive), \(\sigma_L^P\) = surface tension liquid (polar), \(\sigma_S^D\) = surface free energy solid (dispersive), \(\sigma_S^P\) = free surface energy liquid (polar), \(\sigma_L\) = overall surface tension liquid, \(\theta\) = measured contact angle liquid/solid interface. In order to determine the surface energy we tested the solid surface using a liquid which exhibits only a dispersive component to its overall surface tension (\(\sigma_L = \sigma_L^D = 50.8 \text{ mN/m}\) featuring a high surface tension, hence diiodmethane (\(\sigma_L^P=0\)) was the solvent of choice. Straightforward, eq. (1) reduces to:

\[\sigma_S^D = \frac{\sigma_L(\cos\theta + 1)^2}{4}\]  

(2)

\(\sigma_S^D\) can be directly determined from the measured CA of diiodmethane. In the next step, we proceeded with measuring the CA of distilled water showing one polar and one dispersive component to its overall surface tension (\(\sigma_L^P = 46.4 \text{ mN/m}, \text{ and } \sigma_L^D = 26.4 \text{ mN/m}\)). Knowing these components, we calculated \(\sigma_S^P\) as the only unknown parameter in eq. (1). By adding the dispersive and the polar components on the solid, we finally obtained the \(\sigma_S\) overall surface energy of the M-CAT-1 materials (equation 3):

\[\sigma_S^D + \sigma_S^P = \sigma_S\]  

(3)
Table S1. overall surface energies ($\sigma_S$) and the respective dispersive ($\sigma_D^S$) and polar component ($\sigma_P^S$) estimated for Ni- and Co-CAT-1 oriented and compact films (OCF) and oriented and nanostructured films (ONF).

| M-CAT-1        | $\sigma_S$ [mN/m] | $\sigma_D^S$ [mN/m] | $\sigma_P^S$ [mN/m] |
|----------------|-------------------|---------------------|---------------------|
| Ni-CAT-1 (OCF) | 71.37             | 50.8                | 20.4                |
| Co-CAT-1 (OCF) | 73.6              | 50.8                | 22.8                |
| Ni-CAT-1 (ONF) | 79.5              | 50.8                | 28.5                |
| Co-CAT-1 (ONF) | 79.5              | 50.8                | 28.5                |
4. Reference contact angle measurements

CA measurements on gold substrates

Figure S4.1 A) CA measurements of a bare gold surface after preparation in air with water as test liquid. B) CA measurements of a bare gold surface after preparation in water with dichloromethane as test liquid C) Macroscopic photographs of water droplets for the CA measurements in air placed on a bare gold surface.

CA measurements on glass substrates

Figure S4.2 A) CA measurements of a bare glass surface in air with water as test liquid. B) CA measurements of a bare glass surface after preparation in water with dichloromethane as test liquid C) Macroscopic photographs of water droplets for the CA measurements in air placed on a bare glass surface.
5. Characterization of M-CAT-1 thin films

Oriented and compact Ni- and Co-CAT-1 thin films

Figure S5.1 A), C) and E) Depicting the GIWAXS measurements of an oriented and compact Ni-CAT-1 film on gold, top-view SEM and 30° tilted SEM cross-section image of the same sample, respectively. B), D) and F) Depicting the GIWAXS measurements of an oriented and compact Co-CAT-1 film on gold, top-view SEM and 30° tilted SEM cross-section image of the same sample, respectively.
Figure S5.2 Atomic force microscopy topographic image of a 1.2 um x 1.2 um area of an oriented and compact Ni-CAT-1 thin film. Measured roughness Rms of 9.8 nm.

Figure S5.3. Atomic force microscopy topographic image of a 1.2 x 1.2 area of an oriented and compact Co-CAT-1 film. Measured roughness Rms of 16.3 nm.
Nanostructured Ni- and Co-CAT-1 thin films on gold substrates

Figure S5.2 A), B) and C) Depicting the cross-section, a magnified cross-section image, and a top-view micrograph of Co-CAT-1 grown on gold as a nanostructured surface, respectively. D), E) and F) Depicting the cross-section, a magnified cross-section image, and a top-view micrograph of Ni-CAT-1 grown on gold as a nanostructured surface, respectively.

Water and oil-contact angles of compact and oriented Ni-CAT-1 films

Figure S5.3 Cross-section SEM micrographs of A) an oriented and compact Ni-CAT-1 film and B) an oriented (pillar-like) nanostructured Ni-CAT-1 film. C) and D) WCA of the compact (WCA = 32°) and the nanostructured (WCA = 0°) films. E) and F) Underwater OCA of the compact (CA = 133°) and the nanostructured film (CA = 173°) with dichloromethane (DCM).
Figure S5.4 An image series of a self-cleaning surface experiment (3 fps) with DCM as an oil droplet placed on the nanostructured Ni-CAT-1 film performed at a substrate tilt angle of 1.4°

Photographs of the WCA and OCA measurements

Figure S5.5 A) and B) Macroscopic macrographs of the WCA measurements on compact Co- and Ni-CAT-1 films. C) and D) WCA measurements of nanostructured Co and Ni-CAT-1 films in water. E) and F) OCA measurements of nanostructured Co- and Ni-CAT-1 films in water.

GIWAXS and SEM analysis of nanostructured films grown on glass substrates

Figure S5.6 A) GIWAXS pattern of a Ni-CAT-1 oriented film grown on a glass substrate. B) Corresponding top-view micrograph of the film.
UV-Vis of nanostructured Ni-CAT-1 films grown on quartz

Figure S5.8 Transmission UV-Vis of the Ni-CAT-1 sample grown on quartz substrates. The material exhibit a strong absorbance with on onset at 425 nm.
6 Anti-fog coating experiments

Macroscopic photograph of the anti-fog coating experiment

Figure S6.1 Macroscopic photographs of the anti-fog coating experiment illustrating the principle set-up. In a glass vessel a hot water bath is provided. The hot steam rising from the hot water reservoir is condensing on the upper part of the glass vessel, while the Ni-CAT-1 coated glass support remains free of water droplets. Therefore, the vision through the glass support remains untouched.

Temperature-dependent anti-fog coating experiments

Figure S6.2 Temperature-dependent anti-fog experiment series. Here, the glass reference and the Ni-CAT-1 film on glass were cooled down to temperature of 10°C, 4°C and -20°C. After cooling, the substrates were placed on top of the hot water reservoir. It can be seen that in all three cases the hot vapor steam is not condensing on the Ni-CAT-1 glass supported samples.
7 Wetting models

Figure S7.1 Scheme of possible wetting models for a liquid of a structured solid surface. **A)** Displays the wetting angle $\theta$ of a theoretical flat surface. **B)** Change of the wetting angle to $\theta_w$ according to the Wenzel equation: $\cos \theta_w = r \cos \theta$. In this model, the structuring of the solid enhances the inherent existing wetting properties of the surface. The liquid is homogenously wetting the surface. **C)** Cassie and Baxter description of the contact angle $\theta_{CB}$ if the liquid is only heterogeneously wetting the surface by only being connected to the elevations on the structured surface.
