

Electronic Supporting Information

## Solvent-free on-surface synthesis of boroxine COF monolayers

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### 1) Experimental details

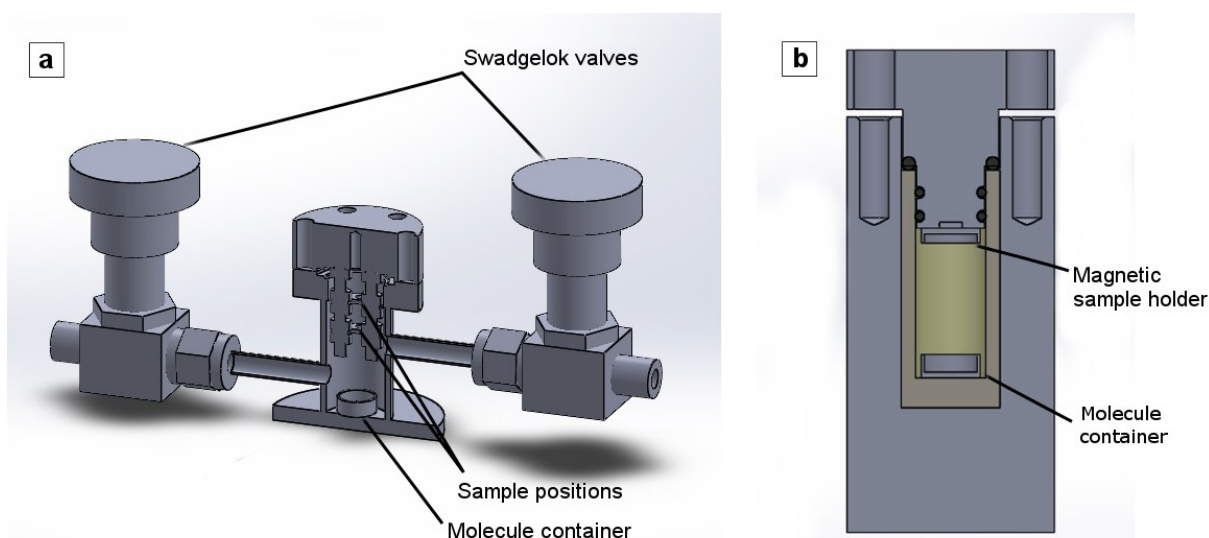
All compounds, 1,4-benzene diboronic acid (**1**), 4,4' biphenyldiboronic acid (**2**), 4,4'biphenyldiboronic acid bis(pinacol) ester (**3**), were obtained from Sigma Aldrich and used as received. For COF-synthesis ultra pure water from Kendall was used.

Scanning Tunneling Microscopy (STM) experiments on COF monolayers were performed with a home-built instrument with integrated nano-positioner driven by a ASC 500 SPM controller (attocube systems AG, Munich, Germany). STM images were acquired under ambient conditions on dry samples in constant current mode with mechanically cut Pt/Ir tips (90/10, 0.25 mm diameter). Images were processed using Gwyddion software (leveled and in some cases noise filtered).

STM experiments on self-assembled monolayers of **3** were carried out in ultra-high vacuum at a base pressure of  $\sim 2 \times 10^{-10}$  mbar with a home-built instrument driven by a Nanonis BP4 SPM control system (SPECS Zurich, Switzerland). Images were acquired at room temperature in constant current mode with electrochemically etched tungsten tips. Epitaxially grown thin films on mica (Georg Albert PVD, Silz, Germany) were used as Au(111) substrates, and prepared in-situ by cycles of Ar<sup>+</sup>-ion sputtering and annealing at  $\sim 490$  °C. The pinacol boronate ester **3** was evaporated onto clean Au(111) from a Knudsen cell at a crucible temperature of 120°C for 10 minutes.

Scanning Electron Microscopy (SEM) images were acquired with an Evo MA15 (Carl Zeiss Microscopy GmbH, Jena, Germany). All images shown are secondary electron images. Samples were measured as prepared by either drop-casting or vapor-deposition without any additional treatment. Images were acquired at 20 kV beam voltage with an electron current of 15 pA in optimized working distances.

Evaporation rates of **1** and **3** were measured by means of a water-cooled Quartz Crystal Microbalance and a home-built Knudsen cell. AT cut quartz crystals with a nominal resonance frequency of 6.0 MHz and a Q-pod quartz crystal monitor (Inficon GmbH, Köln, Germany) were used. The measured frequency shifts  $\Delta f$  were converted into layer thickness  $d$  using the Sauerbrey equation and assuming a typical density of 1.5 g/cm<sup>3</sup> for the organic layers. Van't Hoff plots were derived by plotting the logarithm of the deposition rate  $\ln(\Delta d/\Delta t)$  vs. reciprocal crucible temperature  $T^{-1}$ .



**Fig. S1** Sketch of both reactors applied for COF-synthesis. The reactor shown in (a) with valves was mainly utilized for drop-casting synthesis; the closed reactor shown in (b) was used for vapor-deposition synthesis.

Two different reactors were used for the polymerization as shown in Fig. S1. Drop-casting experiments were performed in an open reactor. Therefore ~8  $\mu$ L supersaturated solution of **1**, **2** or **3** in nonanoic acid or heptanoic acid were applied onto graphite (0001). These samples were placed face-up into the stainless-steel reactor shown in Fig. S1(a) (volume ~ 7.7cm<sup>3</sup>) with ~50  $\mu$ L ultra pure water added to the reactor bottom, not in direct contact with the samples. The reactor valves were left ¼ turn open in order to enable gas exchange with the environment and ensure that the interior remained at atmospheric pressure.

In-situ vapor-deposition synthesis with monomers **1** and polymerization of ex-situ vapor-deposited monomers **3** were mainly performed in the closed stainless-steel reactor shown in Fig. S1(b) (volume ~ 3.2 cm<sup>3</sup>) with the samples face-down.

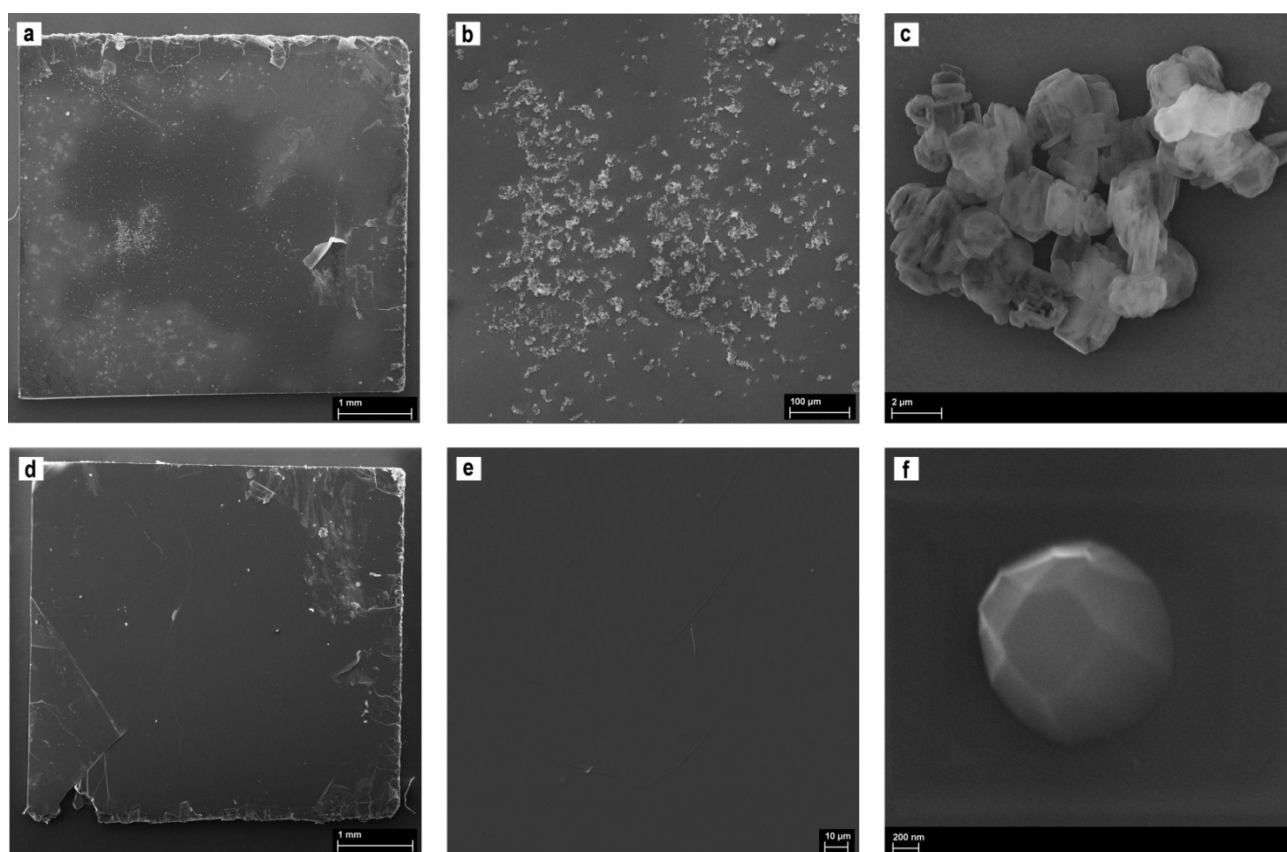
For COF-1 monolayer synthesis the reactor was charged with monomers **1** (~ 3 mg) added to a small container at the bottom, water (~ 17  $\mu$ L), and freshly cleaved graphite as substrate (~ 25 mm<sup>2</sup>). Direct contact of either monomers or graphite substrates with the added water was avoided. The reactor was then heated up to 130 °C in 15 minutes, held at this temperature for 2 h, slowly cooled down to 80 °C in 30 minutes, and then left to cool down to room temperature. The idea of the slow cooling step is staying close to equilibrium while the reaction conditions change from reversible to irreversible.

For COF monolayer synthesis from **3** without any solvent, the monomer was deposited in UHV by thermal sublimation onto graphite at a crucible temperature of 135 °C for 30 minutes. Prior the graphite substrate was cleaned in-situ by annealing at 300 °C. Subsequently, the samples were taken

out of UHV and further processed under ambient conditions, i.e. heated to 160 °C in the closed reactor charged with ~27  $\mu$ L liquid water for 3 hours.

Additional vapor deposition experiments were also performed in the closed reactor with slightly adapted water volumes (~25  $\mu$ L) and temperatures (130-140°C) in case of **1** and ~35  $\mu$ L water and 140 - 150°C in case of **3**.

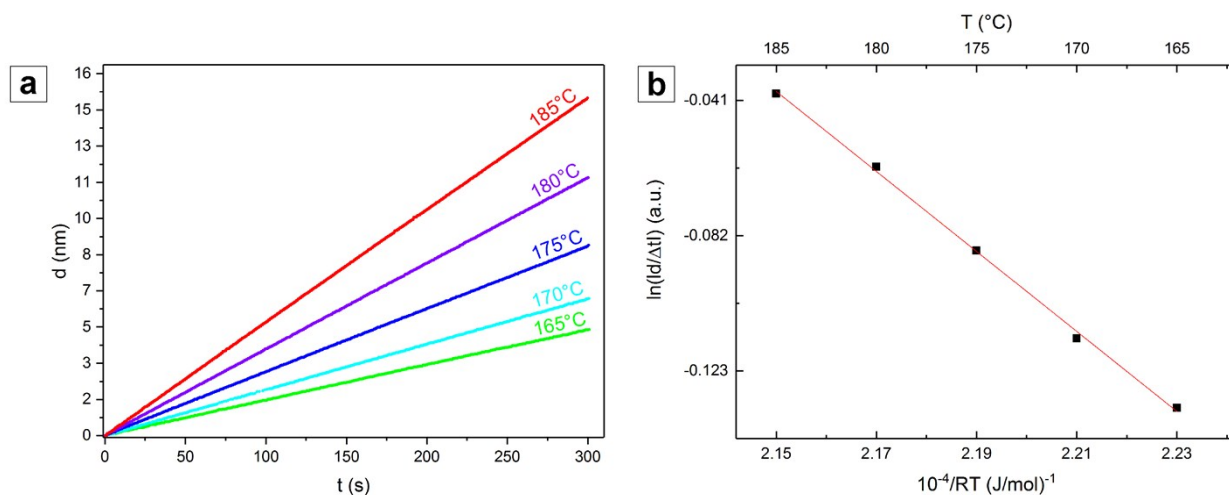
## 2) Additional SEM images



**Fig. S2** SEM images of COF monolayers prepared from **1** on graphite (0001) by either (a)-(c) drop-casting (working distance = 21.5 mm) or (d)-(f) vapor-deposition; working distance = 25 mm for (d) / (e) and working distance = 5.5 mm for (f); Images of the entire sample (a) / (d) show large-scale contaminations for drop-casted samples, whereas at this magnification vapor-deposited samples are free from directly discernible contaminations.

### 3) Sublimation enthalpy of 1,4-benzene diboronic acid

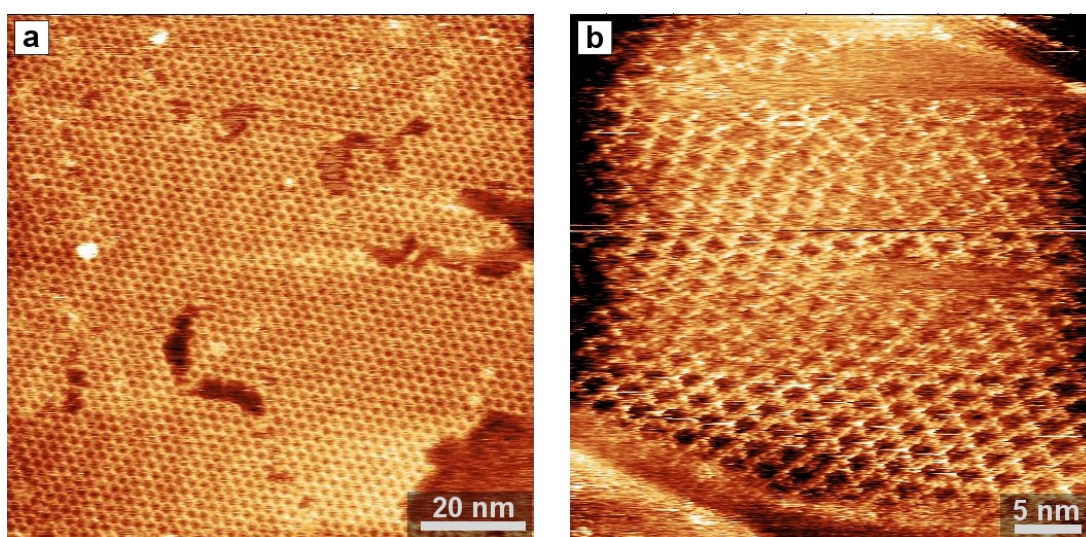
The sublimation enthalpy of **1** was similarly determined in high vacuum sublimation experiments with a QCMB, according to the procedure described above.



**Fig. S3** Sublimation experiments with **1**; (a) QCMB measured thickness  $d$  vs. time  $t$  traces for crucible temperatures from 165 °C to 185 °C in increments of 5°C. (b) Corresponding Van't Hoff plot, resulting in a sublimation enthalpy of  $(207.1 \pm 14.4 \text{ kJ mol}^{-1})$ .

#### 4) Drop-casting synthesis with boronate pinacol esters

Preliminary experiments aimed to clarify the conditions for the conversion of boronate pinacol esters into free boronic acids by on-surface hydrolysis. Therefore COF monolayers were prepared by drop casting 4,4'-biphenyldiboronic acid bis(pinacol) ester (**3**) from heptanoic acid solution and subsequent polymerization, i.e. heating in a water atmosphere. As shown in Fig. S4(a) this procedure afforded COF monolayers. In STM experiments the pinacol boronate ester-derived COFs were indistinguishable from those prepared by drop-casting 4,4' biphenyldiboronic acid (**2**), shown in Fig. S4(b) for comparison. These experiments indicate that hydrolysis already takes place under typical polymerization conditions, i.e. temperatures and water partial pressures.



**Fig. S4** STM images of COF monolayers prepared by drop-casting (a) boronate pinacol ester **3** ( $V_{\text{bias}} = 650$  mV,  $I_t = 52$  pA). (b) the corresponding diboronic acid **2** ( $V_{\text{bias}} = 600$  mV,  $I_t = 51$  pA).