

Postsynthetic Functionalization of 3D Covalent Organic Frameworks

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Supporting Information

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I. Materials and Instrumentation

Materials. All reagents were obtained from Sigma-Aldrich (Milwaukee, WI). Toluene, tetrahydrofuran, was obtained from a custom designed solvent purification system employing activated alumina under argon. Air and water sensitive reactions were performed on a Schlenk line under a N₂ atmosphere. (Methanetetrayltetra-4,1-phenylene)tetrakisboronic acid (**1**) was made according to a previously reported procedure^[1]. Allyl functionalized tris(boronic acid) (**2**) was synthesized as previously reported.

Instrumentation. Infrared spectra of solid samples were recorded using a Thermo Nicolet iS10 FT-IR spectrometer with a diamond ATR attachment and are uncorrected.

NMR spectra were recorded on a Varian INOVA 500 MHz spectrometer using a standard ¹H{¹³C, ¹⁵N} Z-PFG probe with a 20 Hz sample spin rate. ¹H NMR spectra for quantitative determination of capping agent were acquired at 500 MHz with a 4 s acquisition time and a 20 s relaxation delay. The integral accuracy was confirmed on a pure sample of compound **2**.

Scanning electron microscopy was done on a LEO 1550 FESEM (Keck SEM) operating at 1.00 kV and a working distance of 3 mm. Samples were prepared by adsorption onto a silicon wafer, which was then attached to a flat aluminum platform sample holder. The sample was then placed directly into the instrument. No metal coating was applied.

Surface area measurements were conducted on a Micromeritics ASAP 2020 Accelerated Surface Area and Porosimetry Analyzer using *ca.* 35 mg samples degassed at 23 °C for 6 h and then 90 °C for 6 h and backfilled with N₂. Nitrogen isotherms were generated by incremental exposure to ultra high purity nitrogen up to *ca.* 1 atm in a liquid nitrogen (77 K) bath and surface parameters were determined using BET adsorption models included in the instrument software (Micromeritics ASAP 2020 V4.00). BET surface area was determined though models included in the instrument software.

Powder X-ray diffraction (PXRD) patterns were obtained on a Rigaku Smartlab X-Ray diffractometer in reflectance parallel beam/parallel slit alignment geometry. The measurement employed Cu K α line focused radiation at 1760 W (40 kV, 44 mA) power

and a Ge crystal detector fitted with a 1.0 mm incident slit. Samples were mounted on zero-background quartz sample holders and flattened with a glass microscope slide. No sample grinding or sieving was done prior to analysis. Samples were observed using a 0.0200° 2θ step scan from $2.0 - 34.0^\circ$ with a scan speed of 5° min^{-1} . No peaks could be resolved from the baseline for $2\theta > 35^\circ$ and this region was not considered for further analysis. Crystallite size was determined by applying the Scherrer equation to the powder patterns based on an alumina standard.

A Spectroline ENF-260C hand-held UV lamp from Spectronics Corporation (Westbury, New York) was used to generate light at 365 nm.

II. Experimental Protocols

Synthesis of COF-102-allyl. Tetrakis(boronic acid) **1** (50.0 mg, 0.101 mmol) and allyl-functionalized truncating agent **2** (0.1 eq – 0.5 eq) were sonicated in 1 mL mesitylene / dioxane (1:1 v/v) in a 20 mL vial until a fine suspension was obtained. The suspension was then transferred by pipet to a pre-scored 5 mL ampoule, flash frozen in $\text{N}_2(l)$, and flame sealed. The ampoule was put in an oven at 90°C for 27.5 h, after which the ampoule was cooled to rt, opened, and the solid was isolated by filtration. The solid was washed with 5 mL dry THF was added and after 30 min, the solvent was then removed by syringe. This process was repeated three times and the COF was subsequently dried under vacuum.

Synthesis of COF-102-SPr. COF-102-allyl (30 mg, 22 mol% allyl) and 2,2-dimethoxy-2-phenyl acetophenone (1 mg, 0.1 eq/allyl group) were added to a dry Schlenk tube under N_2 atmosphere. Dry, degassed THF (0.372 mL) followed by propane thiol (6 mg, 1.1 eq) were subsequently added. The reaction was allowed to stir at 23°C for 18 h under irradiation at 385 nm (Figure 2), at which point the resulting suspension was allowed to settle and the THF was removed. Washing twice with THF yielded COF free of the remaining photodegradation products. COF-102-SPr was subsequently dried under vacuum and isolated as a white, odorless powder.

III. Additional Characterization

Figure S1. FT-IR spectrum of COF-102-allyl and COF-102-SPr

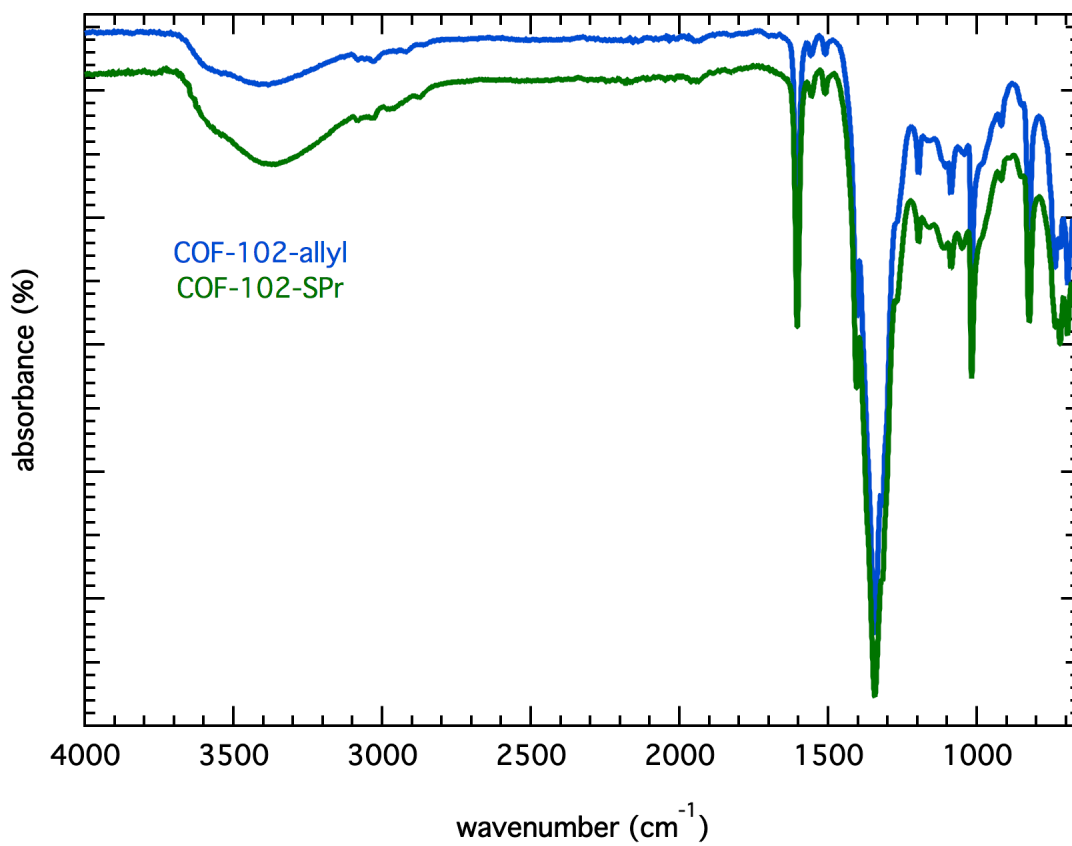


Figure S2. Scanning electron micrographs of COF-102-allyl

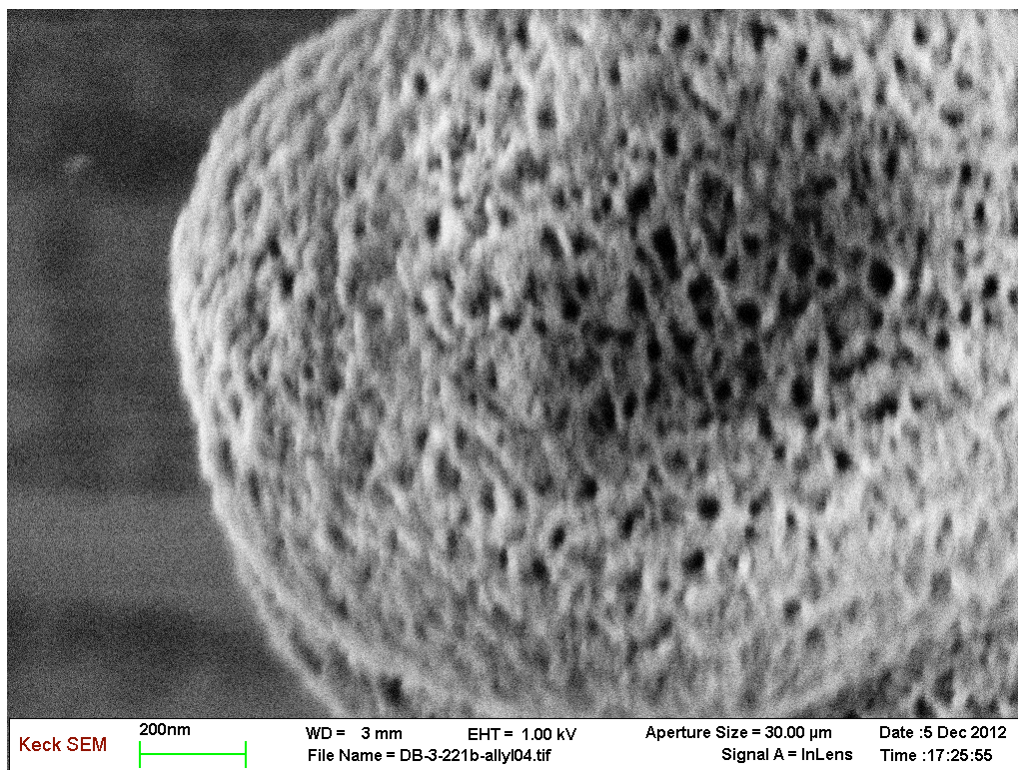
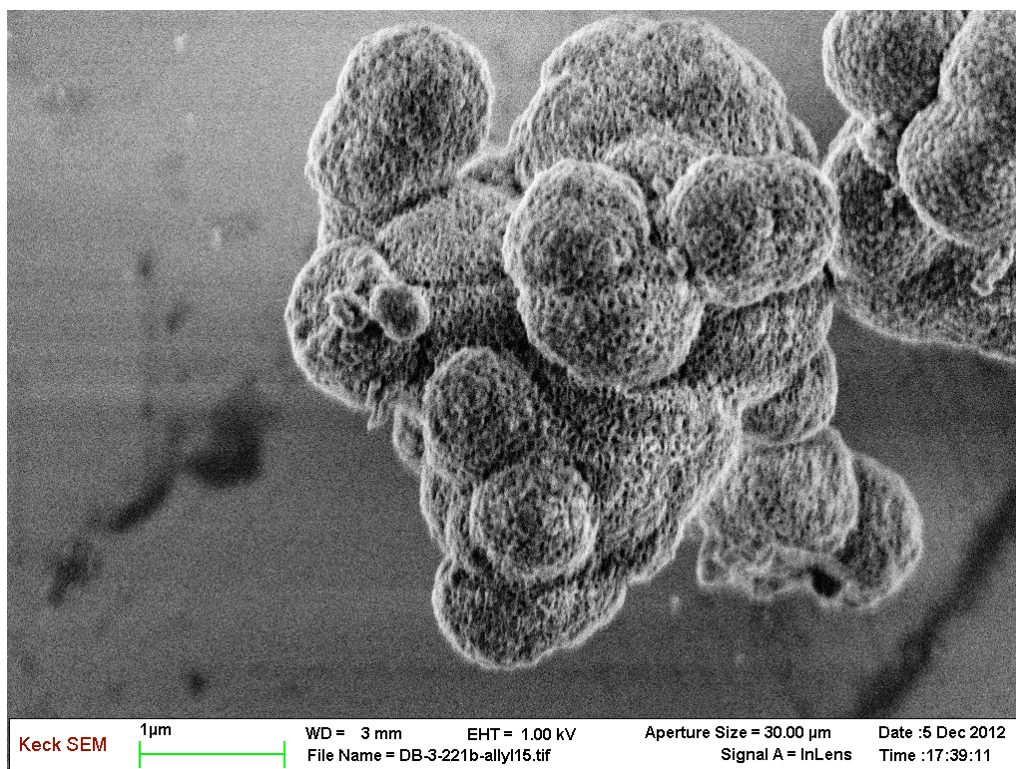


Figure S3. Scanning electron micrographs of COF-102-SPr

