Supporting information

Lewis base mediated efficient synthesis and solvation-like host-guest chemistry of covalent organic framework-1

Suresh Babu Kalidindi,1 Christian Wiktor,1, 2 Ayyappan Ramakrishnan,3 Jana Weßing, Andreas Schneemann, Gustaaf Van Tendeloo,2 and Roland A. Fischer1,*

Materials:
All chemicals were purchased from commercial sources (Sigma-Aldrich, Alfa Aesar, and others) and used without any further purification.

Characterization:
All the samples were handled under inert conditions during the sample preparation.

The infrared spectra were recorded on a Bruker Alpha-P FT-IR instrument in the ATR geometry with a diamond ATR unit inside a glovebox(Ar).

Powder X-ray diffraction measurements were performed in a capillary mode, using a D8-Advance Bruker AXS diffractometer with CuKα-radiation (λ = 1.5418 Å) and a focused Göbel mirror in θ-2θ geometry with a positive sensitive detector. For measurements, the samples were filled into 0.7 mm capillaries in a glovebox, which were subsequently flame sealed.

All the MAS-NMR spectra were recorded on a Bruker DSX 400MHz spectrometer, utilizing ZrO2 rotors of 2.5 mm diameter at 293 K. During measurement the rotors were rotated at 20000 Hz. All NMR(MAS) spectra were measured applying pulse programs written by H.-J. Hauswald at the Department of Analytical Chemistry of the Ruhr-University Bochum. The 11B and 13C spectra were referenced to B(OH)3 and adamantane, respectively. The stator of the used NMR probehead (Bruker MAS VTN 400 WB BL 2.5) contains boron nitride. To remove the signals from the 11B spectra a blank measurement without sample or rotor inside the stator was recorded and subtracted from all shown 11B spectra.

UV-Vis diffuse reflectance spectra were measured using a Harrick praying mantis diffuse reflectance accessory mounted in a Perkin Elmer Lambda 650 UV–Vis spectrophotometer. The samples were diluted with BaSO4.
Thermogravimetric analysis was carried out on Netzsch instrument with heating rate of 5 °C/minute in a temperature range of 30-1000 °C under N₂ flow (99.9999%; flow rate = 300 mL/min).

The N₂ adsorption/desorption measurements were performed on a Quantachrome Autosorp-1 MP instrument at 77 K. The samples were out gassed at 150 °C for 3 h.

Scanning electron microscopy images were taken on LE01530 Gemini FESEM instrument. The samples were prepared by dispersing powders on a carbon tape.

TEM sample preparation: The COF-1 powder was sonicated in acetone. A few drops of the resulting dispersion were put on a 3 mm copper grid covered with a carbon film. BF-TEM images were acquired on a Hitachi H-8100 equipped with a LaB₆ gun. HAADF-STEM images and the electron tomography series were acquired on a FEI Tecnai G2 equipped with a Schottky field-emission gun and a single tilt Fischione tomography holder. Both microscopes were operated at 200 kV. The images for the tomographic series were acquired from -74° to 78° tilt angle with a tilt angle increment of 2°. The tomographic reconstruction was done by using the SIRT algorithm in FEI’s Inspect 3D. The visualization was done with Amira 5.0.

Experimental section:

1) Synthesis of COF-1•NH₃

Benzenediboronic acid (2g, 12.0 mmol) was dissolved in 200 mL of 1,4-dioxane solvent in a 250 mL beaker. This was placed in a desiccator under an atmosphere of 33% NH₄OH (20 mL, ~18 mmol). The reaction was allowed to sit at room temperature for overnight. The reaction mixture was centrifuged for 5 min at 2000 rpm. The white precipitate was washed with acetone and dried under vacuum at room temperature. Yield: ~1.5 g

IR(cm⁻¹): 3807 (W), 3525(VW), 3479(VW), 3387(W), 3340(VW), 3304(VW), 3260(W), 1496(S), 1390(S), 1356(S), 1324(S), 1287(VS), 1202(W), 1110(W), 1072(W), 1009(S), 995(W), 863(W), 834(VW), 700(S), 609(VW).

¹³C NMR(MAS) δ: 147.6, 135.7, 132.0, 130.3 and 68.8 (from solvent, 1,4-dioxane)

¹¹B NMR(MAS) δ: 7, -1, and -9

Elemental analysis:
Elemental analysis calculated for 0.6 NH$_3$ molecules per formula unit of COF-1 i.e. C$_3$H$_2$BO$_{1/3}$NH$_3$

Cal: C: 51.08; H: 4.29; N: 6.62;
Found: C: 52.56, H: 4.9, N: 3.21

The mismatch is due to the partial removal of NH$_3$ from the framework during evacuation at room temperature and presence of 1,4-dioxane solvent.

2) Synthesis of COF-1 from COF-1• NH$_3$

The COF1•NH$_3$ framework (~1.5 g) was heated in a Schlenk tube at 150 °C overnight under dynamic vacuum. Thus obtained COF-1 is stored in a solvent free glovebox (Ar atmosphere). Overall yield: ~1.3 g (83% based on BDBA)

IR(cm$^{-1}$): 1497 (s), 1386 (s), 1353 (w), 1322 (s), 1282 (s), 1246 (w), 1098 (s), 1072 (s), 1010 (vs), 835 (w), 694 (s), 648 (w)

$^{13}$C NMR(MAS) $\delta$: 135.7 (broad)

$^{11}$B NMR(MAS) $\delta$: 7,-1

Elemental analysis for C$_3$H$_2$BO:

Cal: C: 55.56; H, 3.10
Found: C: 54.5, H: 3.75

3) Synthesis of Ferrocene@COF-1

50 mg of activated COF-1 was placed together with 100 mg of ferrocene in a glass tube under vacuum. The tube was stored at 100°C for five days. After that the tube was opened under inert gas conditions and the material was stored in a Argon filled glove box.

Yield: 65 mg

IR (cm$^{-1}$): 1497 (s), 1386 (s), 1353 (w), 1322 (s), 1282 (s), 1246 (w), 1095 (s), 1072 (s), 1010 (vs), 994 (w), 835 (w), 808 (w), 694 (s), 648 (w)

$^{13}$C NMR(MAS) $\delta$: 135.4(broad), and 69.5

$^{11}$B NMR(MAS) $\delta$: 7,-1

Elemental analysis calculated for 0.2 ferrocene molecules per formula unit of COF-1 i.e. C$_8$H$_6$B$_2$O$_2$Fe$_{0.2}$

Cal: C: 57.56, H: 3.6, Fe: 6.69
Found: C: 58.9, H: 3.9, Fe: 7.0
4) Synthesis of azobenzene@COF-1

100 mg of activated COF-1 was placed together with 100 mg of trans-azobenzene in a glass tube under vacuum. The tube was stored at 40°C for 3 days. After that the tube was opened under inert gas conditions and the material was stored in a Argon filled glove box.

*Yield: 147 mg*

*IR (cm⁻¹):* 1497 (s), 1386 (s), 1353 (w), 1322 (s), 1282 (s), 1098 (s), 1072 (s), 1010 (vs), 917 (vw), 835 (w), 767 (s), 694 (s), 680 (s), 648 (w), 539 (w), 517 (w)

*¹³C NMR(MAS) δ: * 153.3(broad), 135.5(broad), 124.426(broad)

*¹¹B NMR(MAS) δ: * 7, -1

Elemental analysis calculated for 0.25 azobenzene molecules per formula unit of COF-1 i.e. C₉H₆.5B₂O₂N₀.5

*Cal: C: 61.67, H: 3.74, N: 4.00*

*Found: C: 62.99, H: 3.81, N:4.34*
Figure S1. IR spectrum of COF1•NH₃ framework
Figure S2. $^{11}$B NMR(MAS) spectra of COF-1, and COF$^\cdot$NH$_3$ framework

Figure S3. $^{13}$C NMR(MAS) spectra of COF-1, and COF$^\cdot$NH$_3$ framework
**Figure S4.** TGA profile of COF1•NH3 framework

**Figure S5.** IR spectrum of COF-1 obtained from COF1•NH3 framework
Figure S6. N$_2$ adsorption/desorption isotherm (77 K) of COF-1 obtained from COF1•NH$_3$ framework.
Figure S7. BET plot of COF-1 obtained from COF1•NH$_3$ framework.
Figure S8. BJH pore distribution of COF-1 obtained from COF1•NH₃ framework.
**Figure S9.** SEM images of COF-1 obtained from COF1•NH$_3$ framework at low (top) and high magnifications (down).
**Figure S10.** HAADF-STEM image of COF-1 spheres made of COF-1 platelets. The image shows almost pure mass thickness contrast. Since there is no other material present, and diffraction contrast is absent, the brighter contrast has to originate from the platelets in parallel orientation to the beam.
Figure S11. Characterization of ferrocen@COF-1 inclusion compound; signals from ferrocene are shown with "*". a) IR spectra, b) $^{13}$C NMR(MAS), c) $^{11}$B NMR(MAS) and d) TGA profiles.
Figure S12. Characterization of azobenzene@COF-1 inclusion compound; signals from azobenzene are shown with ‘*’. a) IR spectra, b) $^{13}$C NMR(MAS), c) $^{11}$B NMR(MAS) and d) TGA profiles.