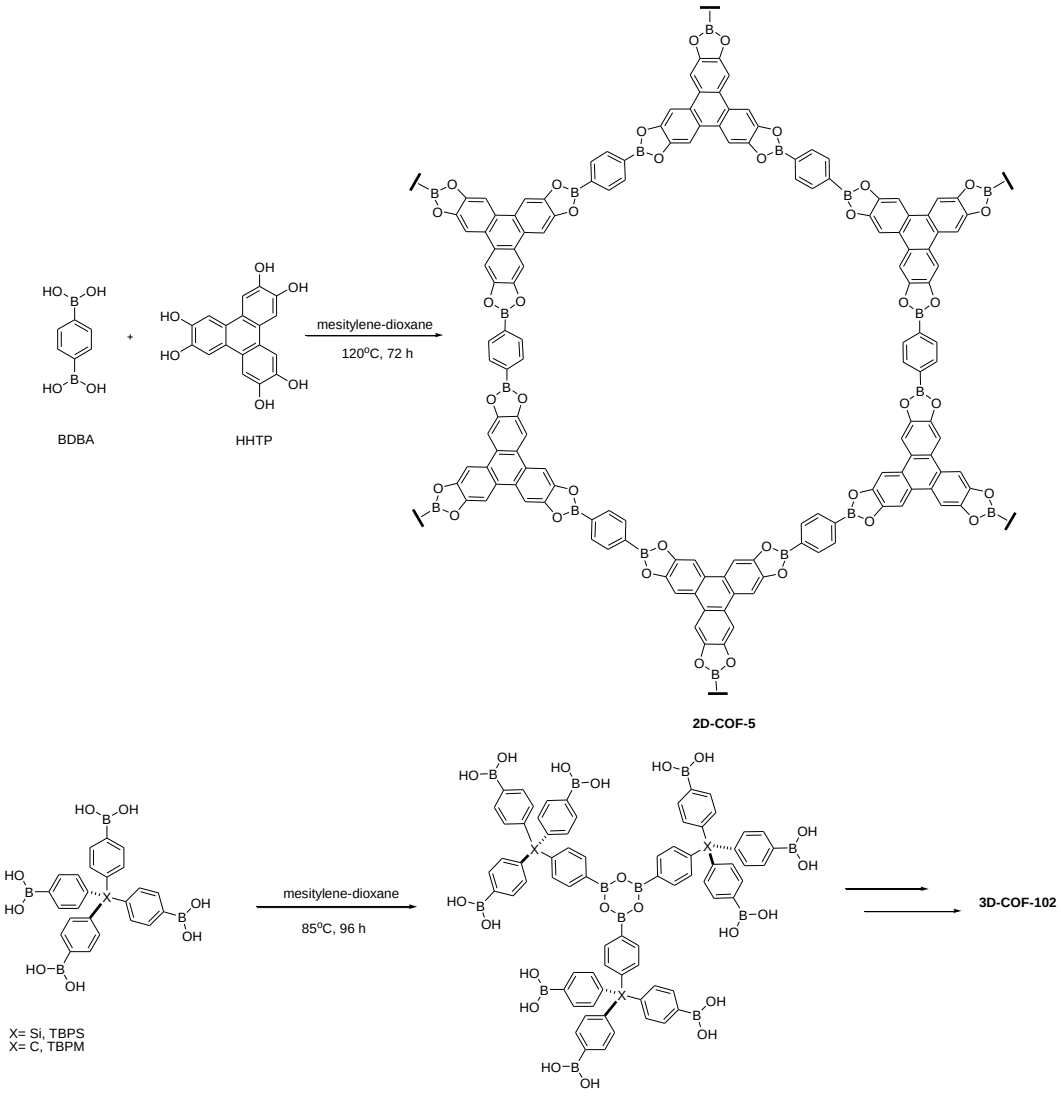
Microwave Synthesis and Purification of Covalent Organic Frameworks

The chemistry of Covalent Organic Frameworks (COFs) is interesting yet underdeveloped. Typically COFs consist of low molecular weight elements such as boron, nitrogen, carbon, and oxygen, which form strong, covalent bonds similar to those in graphite and diamond. This networking imparts unique characteristics, among them high thermal stability sometimes up to 600 °C. Unlike hydrocarbon organic frameworks, heteroatomic frameworks have greater flexibility in their uses because they can be functionalized for gas storage devices, as photonics, and as catalysts. Original work conducted by Professor Omar Yaghi and co-workers details the synthesis of crystalline COFs consisting of carbon, boron, and oxygen, as shown in Scheme 1. Dehydration of diboronic acid (BDBA) and hexahydroxy triphenylene (HHTP) in mesitylene/dioxane at 120 °C for 72 h furnished **COF-5**[1], while self-condensation of tetra(4-dihydroxyborylphenyl)methane (TBPM) and its silane derivative TBPS by heating in mesitylene/dioxane at 85 °C for 96 h produced **COF-102**.[2]

Scheme 1. Synthesis of COFs **5** and **102**



Yields were consistent at 70 – 80% but the reaction times were considerably long, taking anywhere from three to four days. Enter Dr. Neil Campbell, Dr. Lyndsey Ritchie, Mr. Rob Clowes, and Professor Andrew Cooper at the University of Liverpool.[3] Their research demonstrated that the reaction time could be reduced from days to an hour. **COF-5** was prepared in a similar manner as before, except microwave irradiation was used as the heating source. The sample was heated in mesitylene/dioxane at 100 ^{o}C using 200 W for 20 minutes in a CEM Discover® S-Class system with camera attachment (Figure 1a); the camera accessory allows for direct visual access to the vessel during the reaction. The purple supernatant (this was attributed to the formation of oxidized HHTP) was removed after the reaction was complete, and the product was purified via microwave extraction which consisted of microwaving the COF in dried acetone at 55 ^{o}C using 200 W for 20 minutes. The extraction was repeated to give a colorless supernatant, as shown in Figure 1b, and a light grey powder in 68% yield. XRD was obtained and confirmed that microwave synthesized **COF-5** was crystalline and comparable to that of the conventional route, which required three days to synthesize.

a)

b)

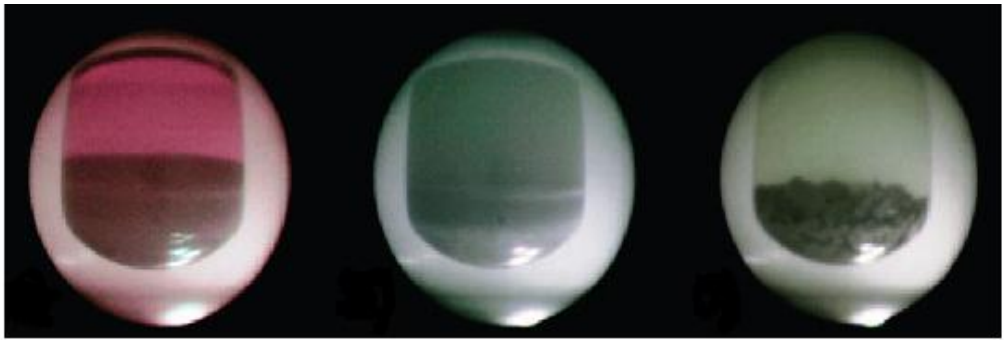


Figure 1. (a) Discover S-Class microwave synthesizer with camera attachment; (b) images captured with the camera attachment. Images were taken inside the cavity. Left, synthesis of **COF-5**; middle, after first extraction; right, after second extraction.[4]

Researchers repeated the microwave synthesis under open vessel microwave conditions and found that the surface characteristics of the COF were similar to that of the sealed vessel reactions, but the yield was increased to 95 %. **COF-102** was also synthesized using microwave irradiation in only one hour. Self condensation of TBPM in mesitylene/dioxane at 100 ^{o}C using 200 W for 20 minutes followed by extraction in THF gave a white powder. A comparison summary, Table 1, presents the time, yield, and surface characteristics of the COFs via microwave irradiation and conventional heating.

Table 1. Time, yield, and surface area of microwave and conventionally synthesized **COF-5** and **COF-102**

COF	Heating Mechanism	Temperature (^{o}C)	Time (h)	Yield (%)	S_{bet} m^2g^{-1}
COF-5	Conventional (sealed)	120	72	71 - 73	1590
COF-5	Microwave (sealed)	100	1 (including extractions)	68	2019
COF-5	Microwave (open)	100	1 (including extractions)	95	2027
COF-102	Conventional (sealed)	85	96	63	3472
COF-102	Microwave (sealed)	100	1 (including extractions)	n/a	2926

In conclusion, COFs synthesized in the Discover S-Class proceeded over 200 times faster than conventional conditions while at similar temperatures. The surface area of **COF-5** was greater when the microwave was used and framework analyses between the COFs prepared via microwave irradiation and conventional conditions were comparable. This incredible work by Professor Cooper and co-workers shows just how microwave irradiation can drastically increase product output by decreasing reaction times.

References

1) Cote, A. P.; Benin, A. I.; Ockwig, N. W.; O'Keeffe, M.; Matzger, A. J.; Yaghi, O. M. *Science* **2005**, *310,* 1166 – 1170. DOI: 10.1126/science.1120411
2) El-Kaderi, H. M.; Hunt, J. R.; Mendoza-Cortes, J.; Cote, A. P.; Taylor, R. T.; O'Keeffe, M.; Yaghi, O. M. *Science* **2007**, *316,* 268 – 272. DOI: 10.1126/science.1139915
3) Campbell, N. L.; Clowes, R.; Ritchie, L. K.; Cooper, A. I. *Chem. Mater*. **2009**, *21*, 204 – 206. DOI: 10.1021/cm802981m
4) Reprinted with permission from Campbell, N. L.; Clowes, R.; Ritchie, L. K.; Cooper, A. I. *Chem. Mater*. **2009**, *21*, 204 – 206. Copyright 2009 American Chemical Society