RUHR-UNIVERSITÄT BOCHUM

RUB

How to build a MOF on

Introduction

MOF+ is a platform which enables the creation of a MOF from two or more building blocks (BBs) and a net. The user is able to search for the desired BB in the library or to draw a custom BB using a sketcher canvas. The BB can be stored in the shopping cart for later use.

Nets can be found either via coordination search or connectivity search. With coordination search, the User can only set the connectivity number of the BBs, whereas for with connectivity search the User can specify the connectivity of the building blocks, i.e. which BBs are connected together. An Advanced Search option is also available.

1 Using the search functions

1.1 How to search for Building Blocks

Building Blocks are classified as organic or inorganic. Each category is further divided by the coordination number. Building blocks can be stored for later use by clicking on the cart icon and can be accessed to under myBBs.

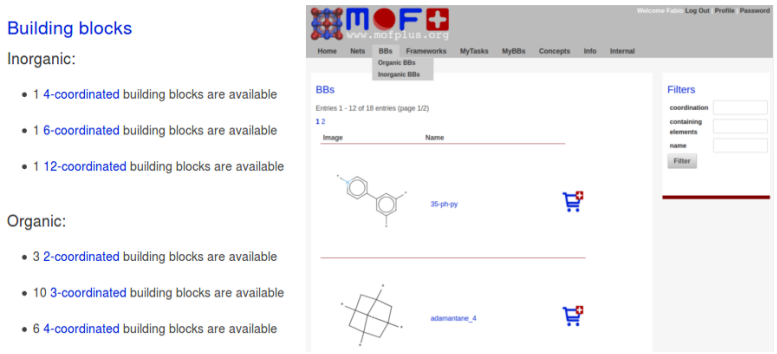

Figure 1: Building Blocks divided by coordination number and search window for organic BBs.

1.2 How to create a Building Block

New BBs can be generated with the help of the JSME editor. A molecule is constructed, and to each coordination site a methyl group is added. Using the nonstandard atom functionality (X on the heteroatoms list) the methyl groups are transformed into coordination sites. In order to do this, the nonstandard atom is set to *:

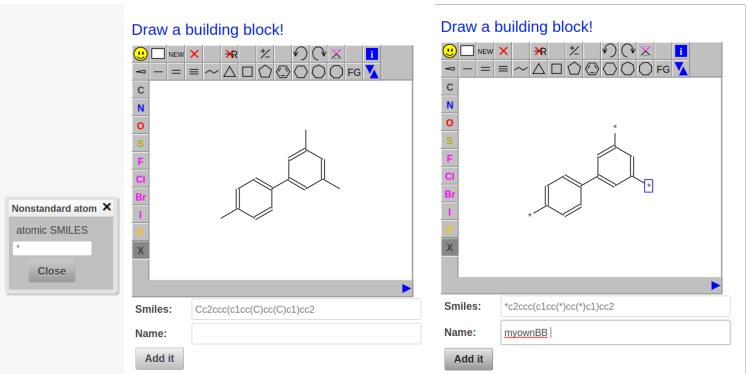

Figure 2: Set nonstandard atom to * and click on the methyl groups to assign connectivity.

After assigning a name, the BB is added to the library by clicking on the **Add it** button. The BB is now available to be used in the construction of MOFs.

1.3 How to search for a net

Depending on the access level of the user there exist up to three different search methods, the coordination search, the connectivity search and the vertex based search. Every method provides basic search options like search by name, by spacegroup number and by transitivity. An explanation of the search criteria is available by clicking on the ? symbol.

1.3.1 Coordination Search

Unregistered users can search nets based on the coordination of the BBs. The connectivity numbers are separated by a comma.

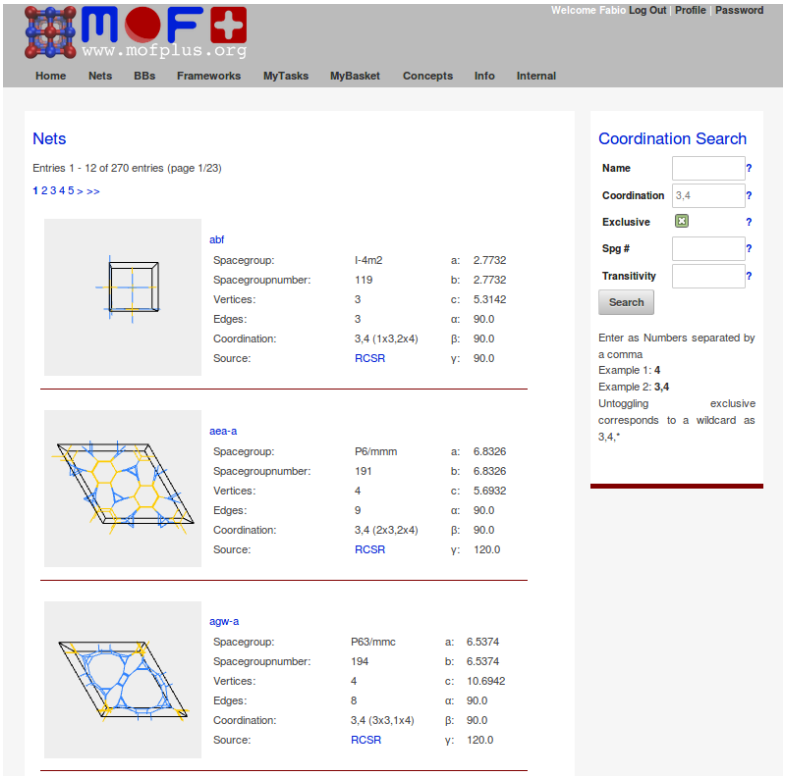

Figure 3: Coordination Search

For example, searching for 3,4 will yield all nets which have building blocks with 3 and 4 coordination points.

1.3.2 Connectivity Search

Unlike the RCSR database, which only offers coordination search, MOF+ also features the connectivity search function. This is only available to registered users. Each connection has to be given as two integer values denoting the respective coordination of the vertex, separated by a hyphen -. If for example a 3,4 net with only 3-4 connections is desired, the connectivity input is 3-4. In this way the query processor knows that 3,4 nets featuring only these connections (3-4) but no other (3-3, 4-4) are to be returned.

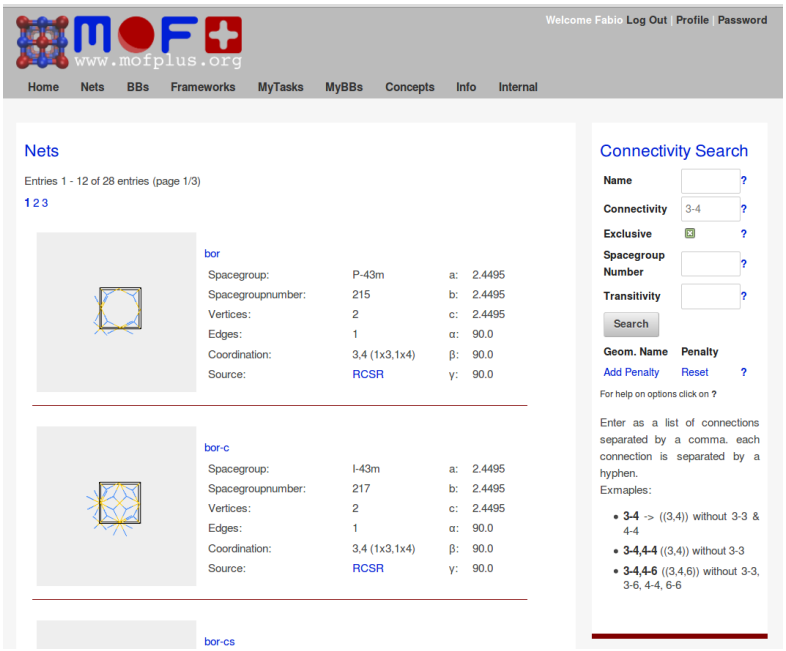

Figure 4: Connectivity Search

1.3.3 Advanced Search

The Advanced Search is the most specific of the search functions, but requires the user to specify more parameters. For a detailed description of the advanced search function please go to **concepts** select **Topologies** from the dropdown list, then click on **"read more"** at the bottom of the page. Alternatively click here: https://www.mofplus.org/content/show/netsearch

2 Weaver

The concept behind the Weaver program is called *reverse topological approach* or RTA. This approach can be used to generate atomistic structures *in silico* starting from two or more BBs and a net:

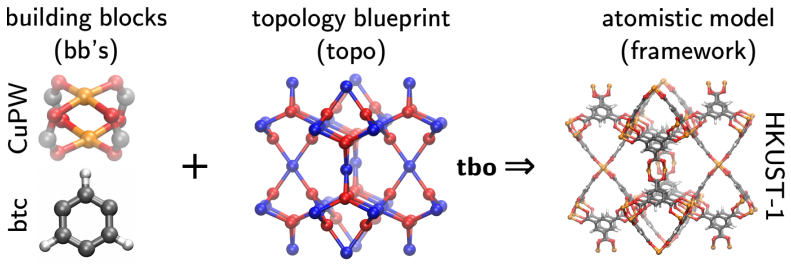

Figure 5: RTA applied to generate HKUST-1.

The set of building blocks already defines possible topologies by Coordination and Connectivity, in the above case a (3,4) net with only 3-4 connections is required. In addition to that the geometry of the vertices of the topology has to match roughly. The four-coordinated vertex should for example not be tetrahedral, but something close to squareplanar .

2.1 How to use Weaver

After adding the desired BBs to the cart and having found a suitable net, the Weaver program can be used to construct a reasonable initial MOF structure, which can be optimized later with a forcefield. The following window will be accessed by clicking on the net name (or double click on the image):

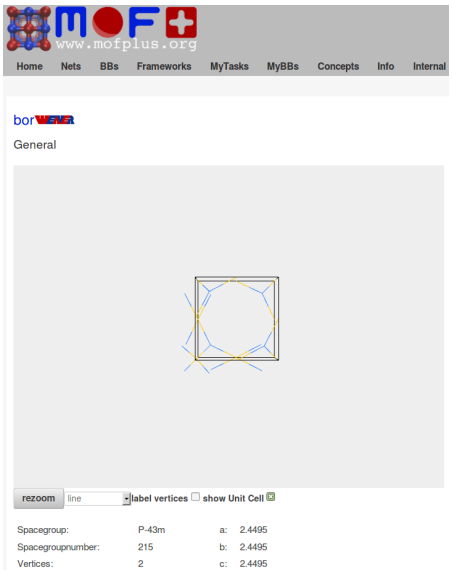

Figure 6: Starting from the net click on the Weaver button next to the name.

By clicking on the WEAVER button on the right of the net name, the following window will be shown:

Figure 7: Weaver setting options: BBs can be assigned to the proper vertices. Click on "Label verices" to see the labelling on the net.

Under **Weaver settings** the User can assign the building blocks to the desired vertices. Only the BBs currently in the cart will be available. After clicking the "Submit" button below the settings, a name will be assigned to the MOF and the following window will be presented:

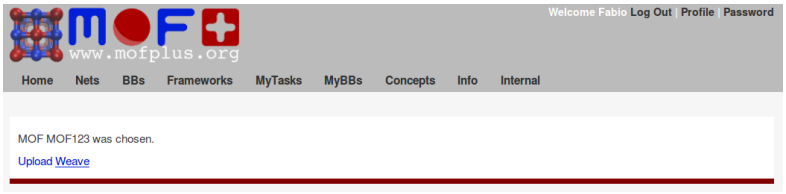

Figure 8: Click on Weave.

After assigning a name to the Weaver run (which will become the name of the structure file), the user can check the status of the optimization under **MyTasks**:

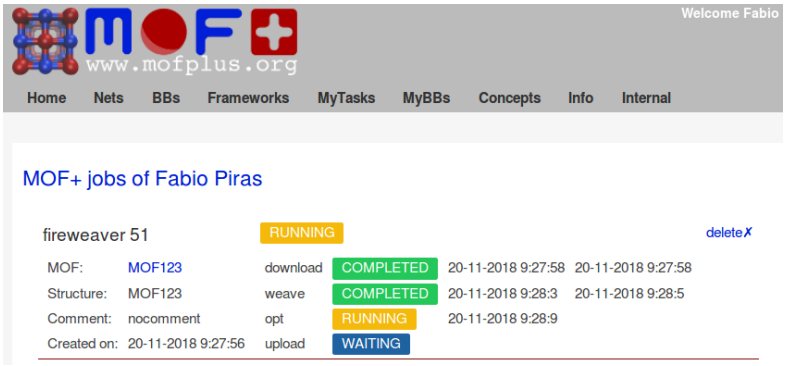

Figure 9: Refresh the browser page to see the progress.

Notice: the weave task usually takes less than 30 seconds. However, the forcefield optimization task may, depending on the size of the structure, take up to 30 minutes!

2.2 Specific connectivity: Pillared BBs as an example

Within MOF+ if the connecting sites of a BB are chemically different, they are assigned specific connectors, as in the case of the interaction between a metal atom and a lone pair (e.g. from nitrogen). There are identical inorganic BBs which only differ in their connectivity, for example CuPW and CuPW-pillared:

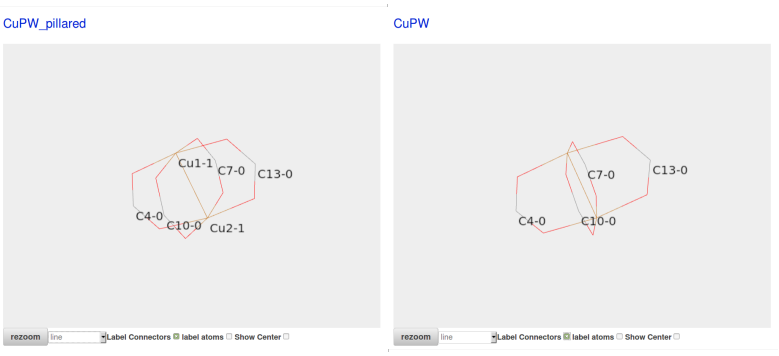

Figure 10: The pillared BB has additional connectivity in the axial positions of the paddlewheel. The specific connectivity of the Cu atoms is 1.

These specific connectivities can be assigned to different BBs as shown in fig. 15. The next section will describe how to use BBs with specific connectivity.

2.3 Colored Nets and Pillared MOFs

If a BB with specific connectors is selected, the User is presented with an additional window during the MOF construction. The following example will use ZnPW-pillared, DABCO and BDC as building blocks to illustrate the procedure:

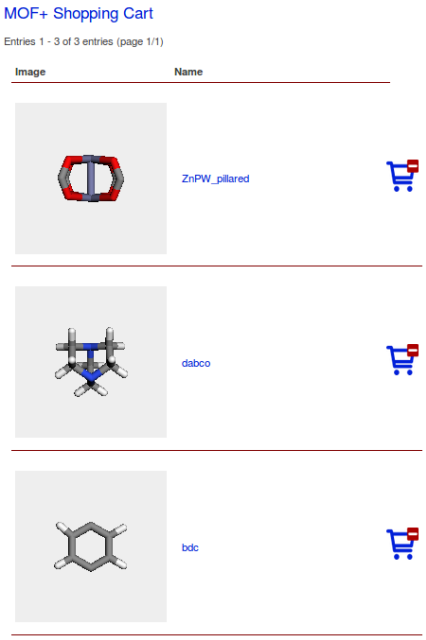

Figure 11: Shopping cart with the BBs used in this example.

The coordination search for (6,2) only yields a specific *coloration* [1] of the pcu net.

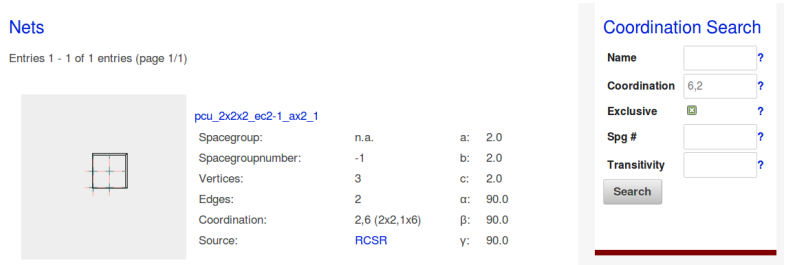

Figure 12: Coordination search results for 6,2.

by clicking on the net name and subsequently on the Weaver button the following window opens:

[1] coloration refers to a specific connectivity pattern that is assigned to a net. For the pcu example, to the four equatorial vertices a specific label or "color" is assigned, whereas the two axial vertices are labeled by a different color.

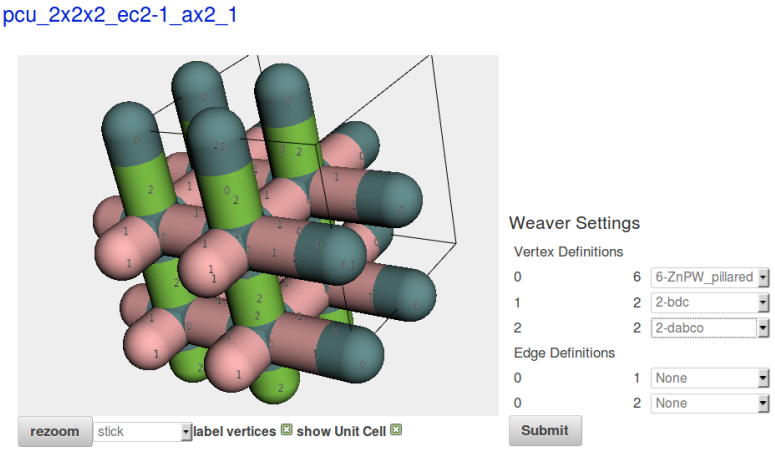

Figure 13: First Weaver settings panel. The colors are better visualized as stick model.

The dark green vertices represent the ZnPW with 6-fold connectivity. The pale green vertices represent the axial ligands, whereas the red ones are the equatorial ligands of ZnPW. It should be noted that there are twice as many red vertices as pale green ones, which matches the connectivity of ZnPW-pillared. Furthermore each vertex has a numerical label: 0 for ZnPW, 1 for the equatorial ligands and 2 for the axial ones.

Given this information, the vertices can now be defined based on the chemical nature of the BBs: the red ligands (vertex 1) are in equatorial position and covalently bound to the carboxylates of the paddlewheel, so the BDC is assigned to vertex 1. Conversely, the pale green ligands (vertex2) are bound to the Zn atoms via coordinative bond though the lone pair of N, therefore DABCO is assigned to vertex 2.

After clicking on **Submit** a second setting window opens:

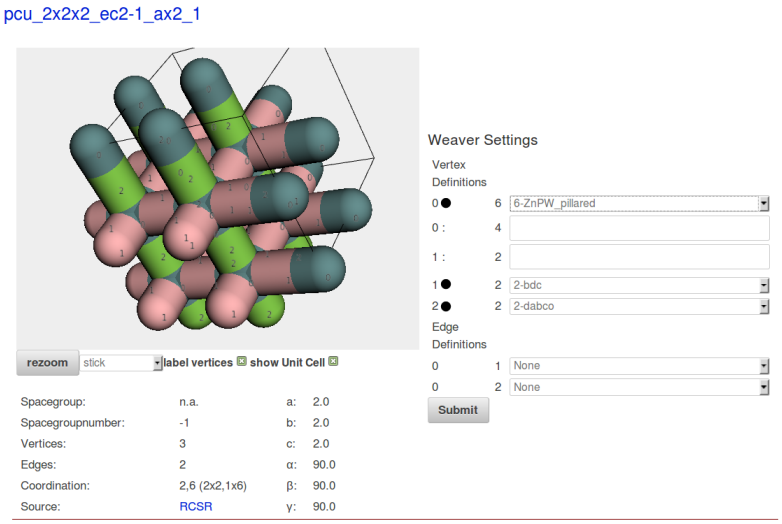

Figure 14: Second settings window.

Step 1: define the vertices without a colon (marked with a black dot on the image): this numbers refer to the coloring of the net! Vertex 0 has 6-fold connectivity and is assigned to ZnPW, Vertex 1 and 2 are assigned to BDC and DABCO respectively, as previously discussed.
Step 2: assign the numbers with colon. Note: the numbers with colon refer to the vertices of the pillared building block (see fig. 10)! Vertex 1 is usually assigned to the metal atom, but the User is encouraged to open the inorganic BB in a new tab and check the vertex assignment. The assignment can also be checked by comparing the connectivity number: vertex 1 has 2-fold connectivity (axial) and vertex 0 has 4-fold connectivity (equatorial).

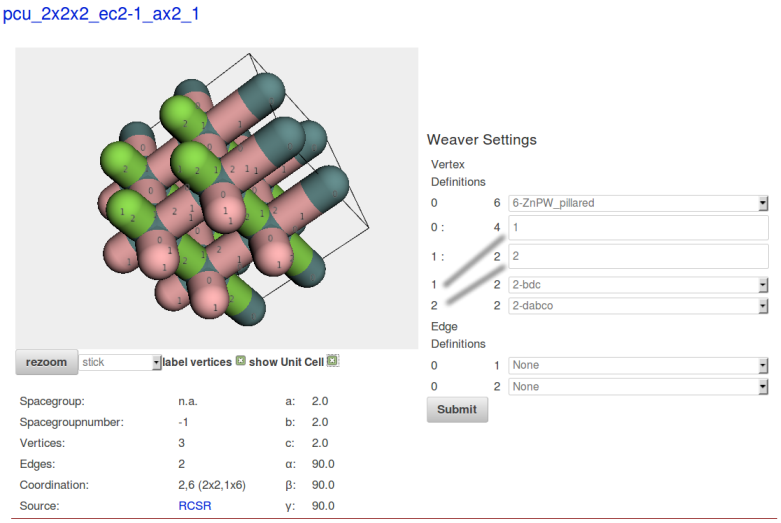

Figure 15: Assign vertices with colon.

0: was assigned to 1 (BDC) and **1:** was assigned to 2 (DABCO). From now on, the previously described procedure is followed.