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"HOW TO" HIGHLIGHT

How to Print a Crystal Structure Model in 3D

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We present a simple procedure for the conversion of Crystallographic Information Files (CIFs) into Virtual Reality Modelling Language (VRML2, .wrl) files, which can be used as input files for three-dimensional (3D) printing. This procedure permits facile production of customized full-colour 3D models of X-ray crystal structures of segments of extended structures, including metal-organic frameworks (MOFs), as well as small molecules. The method uses freely available software that runs under Microsoft Windows, MacOSX and Linux operating systems.

Introduction

Three-dimensional (3D) printing or additive manufacturing is a process of making a three-dimensional solid object of virtually any shape from a digital model. This powerful technology is no longer futuristic, as the cost of 3D printing dropped dramatically over that past decade, making it affordable even to a hobbyist. 3D printing has been touted as ushering "the third industrial revolution"—that of mass customization, wherein virtually any consumer object could be tailored to a previously unprecedented level.[1] This technology will likely revolutionize numerous fields of human activity; as just one example, prosthetic medicine could soon count on implants perfectly matching each individual patient. 3D printing is beginning to affect chemical research as well: Cronin et al. have recently reported the creation of customized 3D-printed "reactionware," the composition and shape of which allow its active participation in the reaction and analysis of products.[2]

Chemistry is full of concepts that require three-dimensional understanding, and representing those in two-dimensional PowerPoint slides, journal articles, or on chalkboards inevitably leads to a loss of detail. Crystallography is even more dependent on 3D representations, and most readers of this journal have likely spent numerous hours turning crystal structure models on their computer screens to produce a view that sacrifices the least information. An ability to easily build 3D models of crystal structures is thus clearly needed. In this contribution, we provide step-by-step instructions on how to convert a .cif file—which is a typical end product of crystal structure refinement—into a 3D-printed physical model of a crystal structure. We use MOFF-3 (Figure 1)—one of our previously published extended metal-organic framework (MOF) structures[3]—as an illustration for this method. This procedure is broadly applicable to many other structures; in our two labs, we have printed 3D models of more than thirty different small molecules and MOFs.

Our procedure is neither the only nor the first method for achieving the conversion of crystallographic information files into 3D printed models.[4] Its advantages are in (*a*) the ability to produce models of both discrete molecules and segments of extended "infinite" structures such as MOFs; (*b*) the use of freely available and highly intuitive software packages (*vide infra*) with ample helpful documentation available online, and (*c*) its reliance on a commercial 3D printing service provided by *Shapeways*, which obviates the need for an in-house 3D printer.

The main disconnect between the crystal structure manipulation programs and 3D printing software lies in the mutual incompatibility of file formats. Out of the commonly used crystal structure processing programs, only PyMOL[5] is able to directly export crystal structure data contained in .cif files into the VRML (.wrl) format most commonly used for colour 3D printing.[6] This feature enable the printing of small molecule models via PyMOL (see Electronic Supporting Information for photos and movies of 3D models of selected small molecules: triazolophanes,[7] cyanostars[8] and a cyanostar-[3]rotaxane). However, many crystal structure processing operations—e.g. connectivity expansion, addition of multiple unit cells, etc.—are rather difficult to do in PyMOL. Our protocol thus resorts to using two programs which together offer greater flexibility in manipulating both the crystal structure and the 3D model. Mercury[9] is used to produce a .pdb file of the crystal structure, which is then imported into Blender[10]—a semi-professional 3D printing program—for additional processing and conversion into a .wrl file. This combination is necessary since Blender appears unable to import .pdb files produced by programs other than Mercury.

Procedure

Four separate pieces of software are required for this conversion: Mercury 3.3,[9] Blender 2.62 and 2.69,[10] and the open-source embedded Python Molecular Viewer (ePMV)

plugin, which runs molecular-modelling software directly in Blender.[11] In our work, we have used Windows versions of these programs as well as MacOSX (Mercury 3.1.1 and Blender 2.62 and 2.70); since all the requisite programs are also available for the Linux operating system, it is reasonable to assume that a very analogous procedure should function on this platform as well.

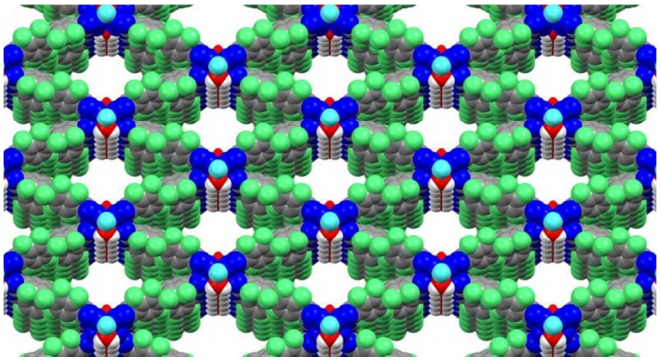

Fig. 1 The starting point: 2D representation of MOFF-3 structure, produced directly from its .cif file using Mercury 3.3.

Instructions are as follows:

1. Set user preferences in Blender 2.62. Open Blender 2.62, then click on *File* > *User Preferences* > *Addons*. Make sure that under *Import-Export* tab, option *Web3D X3D/VRML format* is checked. Under *System* tab, options *autoPack*, *ePMV* and *ePMV synchro* should all be checked. Click on *Save as Default.* As a result, *ePMV* and *autoPACK* buttons will show in the upper right corner of the Blender 2.62 window.
2. Set user preferences in Blender 2.69. Open Blender 2.69, then click on *File* > *User Preferences* > *Addons*. Make sure that under *Import-Export* tab, options *Web3D X3D/VRML format* and *VRML2 (Virtual Reality Modelling Language)* are both checked. Under *Mesh* tab, option *3D Print Toolbox* should be checked. Click on *Save User Settings.*
3. Open the crystal structure's CIF file in Mercury and produce the desired packing (one or more molecules/unit cells). At this stage, it may be also useful if disordered atoms or side chains are deleted, so that only one orientation remains—unless the objective is to highlight the disorder. To delete undesired features of the structure, click on *Edit* > *Edit Structure…* > *Remove*, and then click on atoms or molecules that need to be removed.
4. The resulting data should be saved as a PDB file (*File* > *Save As…*). In our hands, only PDB files produced by Mercury could be successfully used in subsequent steps.
5. Open Blender 2.62 and click on *ePMV* button on the top right. As a result, *ePMV* interface will appear on the left-side panel. Delete the cube, camera, and light objects in the main Blender window (this is done by simply right-clicking on those objects, following by pressing the *Delete* button).
6. In the *ePMV* panel, choose *Browse* and navigate to the PDB file produced in step 4. Upon loading, a series of dots will appear in the main Blender window; these represent individual atoms.
7. In *Atom/Bond Representation* subpanel on the left, choose the desired structural representation; for most organic and inorganic structures, *Atoms* or *Sticks* representations are the most appropriate. The ensuing calculation will take between several seconds and several hours, depending on the complexity of the structure. Values for the *cpk_scale*, *bs_scale*, *bs_ratio*, as well as element colours should be adjusted at this point (if desired), since further changes are not permitted after the file is saved. Changes of these parameters will affect all atoms (or bonds) of a given kind; individual atoms can also be modified using the description given in step 10 below.
8. Save the file and export it as an .x3d file: click on *File* > *Export* > *X3D Extensible 3D (.x3d).*
9. Close Blender 2.62 and open Blender 2.69. Import the .x3d file created in the previous step: click on *File* > *Import* > *X3D Extensible 3D (.x3d).*
10. In *Object Mode*, you can select and delete individual atoms and bonds, and adjust the size of any item (Figure 2, left). For example, to adjust the size of an atom, right-click on the desired atom and choose the *Scale* in the *Object Tools* on the interface on the right. To change the color of atoms and bonds, click on the *Material* icon . Click *(−)* to remove original material and *(+)* to add a new one. The color can be adjusted in the *Diffuse* option. You can rename the material and click F to save it, then apply it to any item that you want to have the same color. This feature is particularly useful if certain parts of the structure need to be emphasized.
11. The produced model will most likely need to be resized to be of dimensions that are practical for printing. To do so, click on the *Scene* button on the right-side panel (third button from the left; highlighted in red in Figure 2, right). Change the *Units* to *Metric*. Then, select all atoms by pressing *A* (with the cursor located in the view window), which should result in the entire structure being highlighted in the main Blender window. Click on *Join* on the left-side panel to connect all of the separate parts, and then use the *Scale* button in the left-side panel to adjust the size of the structure. We have typically found the originally imported structures to be too large, and most of them needed to be scaled down. It should be noted that the dimensions provided by Blender do not correlate well with the size of the printed model (*vide infra*), so adjustment of dimensions for 3D printing requires some trial and error.
12. Once satisfied with the model size, click on the *Object Mode* button on the bottom left and switch the selection to *Edit Mode*. Then, press *W* (with the cursor located in the view window) and click on *Remove Doubles*, which should remove artefact vertices in the structure.
13. Export the resultant data to a VRML2 (.wrl) file: click on *File* > *Export* > *VRML2 (.wrl).*

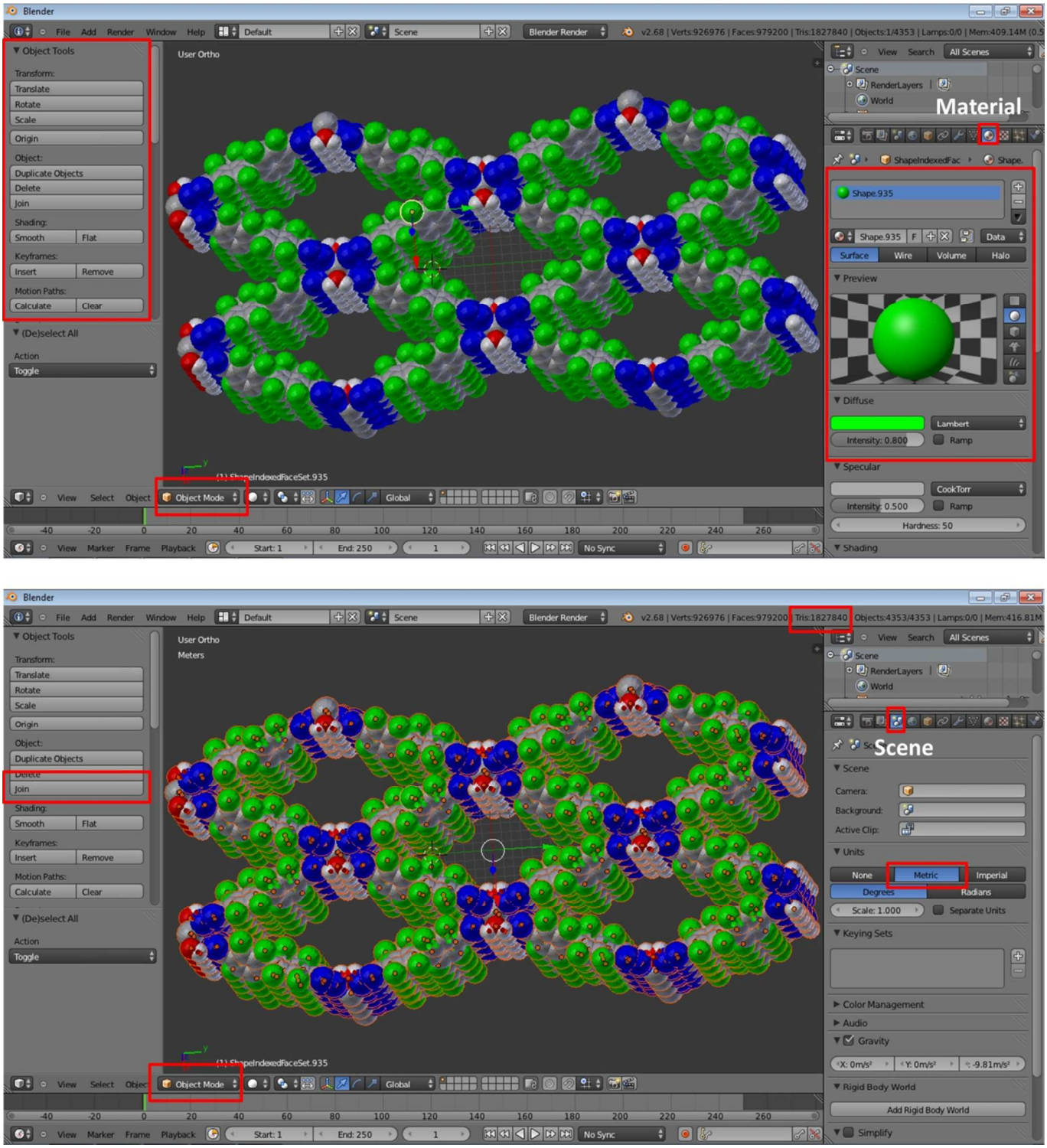

Fig. 2 Exemplary screenshots during the processing of crystal structure data in Blender. Specific buttons required in this procedure are highlighted in red; refer to the text for details.

14. The created .wrl file can now be handled by many commercial and academic 3D-printing facilities. Models presented in this work have been printed by the popular website *Shapeways*.[12] After brief user registration, the source file can be uploaded onto Shapeways website, by clicking on: *Make* + *Sell* > *Upload* > *Select 3D File*, and then choosing the produced .wrl file. Units should be set to inches, and the *Upload Now* button should be clicked. *Shapeways* website will then perform the upload, estimate the model size, and confirm whether the model is indeed printable. The two most commonly encountered problems during the upload are the large file sizes (*Shapeways*

imposes a limit of 64 megabytes, which can be somewhat expanded by uploading compressed ZIP files) and a large number of polygons. The latter are created during the conversion of the structure in Blender and their number can be checked by consulting the *Tris* number on the top-right bar in Blender window (Figure 2, right). *Shapeways* limits the complexity of the uploaded models to 1,000,000 polygons.

15. If the model size is not satisfactory, the model should be scaled again (steps 11 and onward) and the process repeated until a desired size is obtained as the estimate. Once the model size is finalized, the *Shapeways* team will check the printability of the proposed model and inform the user if there are potential issues. If no error is reported, the model can be printed. All that remains is to choose a material for the 3D model. At the time of this writing, *Shapeways* offered a wide variety of plastic, ceramic and metallic substrates (steel, silver, brass, bronze), but the only material offering full-colour functionality was *Full Color Sandstone*, a proprietary mixture of plaster, vinyl polymer, and carbohydates.[13] Incidentally, this is one of the least expensive 3D printing materials offered. If a monochromatic model is desired, we anticipate that most other materials would function well (although we have not tested them).
16. If printability errors are reported, they are most commonly related to the physical limitations of the sandstone material used in the printing. Thus, structures with many bonds may make those bonds too thin (<2 mm) to support themselves; in such cases, either a smaller fragment of the structure should be chosen for printing, or the representation should be switched to Space-filling, with larger *cpk_scale* values used in step 7.

An example of a finished model is shown in Fig. 3. At current (February 2014) prices, a model similar to the one shown in Fig. 3 will cost between $20 and $100 depending on the size.[14] Because sandstone is essentially plaster, models produced from it are rather fragile (they will easily shatter if dropped), thermostable only up to 60 °C, not resistant to water and have grainy surfaces. There are two solutions to the last two problems. First, the printed model can be dipped into a glue (e.g. ZPrinter Z-Bond 90 Infiltrant) to form a coating that gives a strengthened material with a glossy finish when dried. The usage and safety instructions for this product should be followed. For example, when the models are dipped into a plastic container full of the glue, there is a large temperature increase (exothermic) and outgassing is significant enough to warrant the use of personal protective equipment and a ventilated area (fume hood). The model is then patted dry to remove excess glue. The glue penetrates ~2 mm into the model; excess glue will pool and deteriorate the finish. A simpler method that gives similar results makes use of a glossy acrylic spray that can be applied with repetitive spray-dry cycles (4–5 times).

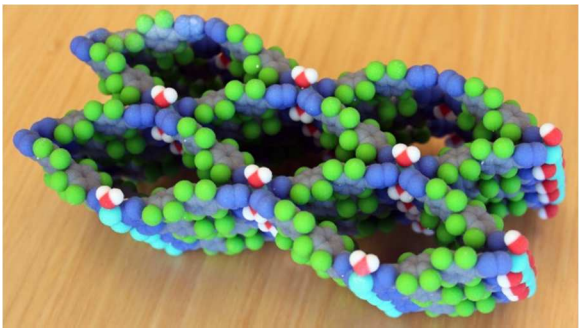

Fig. 3 The finished product: 3D printed model of MOFF-3 structure. Approximate dimensions: 16 × 8 × 7 cm.

Conclusions

In conclusion, we presented here a set of guidelines on how to convert any small-molecule or extended material crystal structure into a 3D printed model. The value of these models should be in facilitating communication of crystal structure details both in the classroom and between experienced practitioners in the field. Our set of instruction uses freely available software, requires no programming knowledge and no knowledge of 3D printing techniques, and produces models using a commercial easy-to-use website.

As with many rapidly developing technologies, we expect these instructions to be outdated within several years, as 3D printers enter the mainstream and crystal structure processing software becomes better integrated with this obviously very relevant technology. Until then, we hope that our colleagues will find this protocol—and its 3D-printed products—useful and educational.

Acknowledgements

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Notes and references

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† Electronic Supplementary Information (ESI) available: [(*a*) sources files (.cif, .pdb, .x3d, .wrl) for all stages of the production of the MOFF-3 3D structure model; (*b*) addendum on 3D printing of dynamic models of supramolecular complexes and mechanically interlocked molecules, and

(*c*) movies of those complexes/molecules in motion]. See DOI: 10.1039/c000000x/

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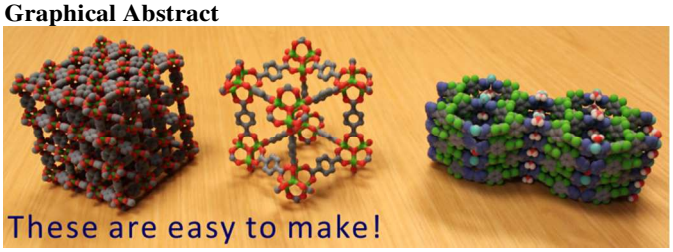
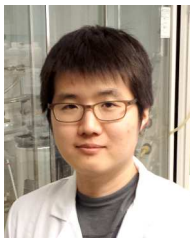
2 (*a*) J. S. Mathieson, M. H. Rosnes, V. Sans, P. J. Kitson and L. Cronin, *Beilstein J. Nanotechnol.*, 2013, **4**, 285–291. (*b*) P. J. Kitson, M. D. Symes, V. Dragone and L. Cronin, *Chem. Sci.*, 2013, **4**, 3099–3103. (*c*) P. Kitson, M. Rosnes, V. Sans, V. Dragone and L. Cronin, *Lab on a Chip*, 2012, **12**, 3267–3271. (*d*) M. D. Symes, P. J. Kitson, J. Yan, C. J. Richmond, G. J. T. Cooper, R. W. Bowman, T. Vilbrandt and L. Cronin, *Nature Chem.*, 2012, **4**, 349–354.
3 T.-H. Chen, I. Popov, O. Zenasni, O. Daugulis and O. Š. Miljanić, *Chem. Commun.*, 2013, **49**, 6846–6848.
4 For examples of printing structures of distinct proteins, see: http://cbe.wisc.edu/assets/docs/pdf/srp-bio/stongrevised.pdf. For small molecules and proteins, see: http://barneybioproductslab.cfans.umn.edu/3d-printing-and-molecular-models/. For a commercial service offering 3D printed molecular models, see: http://models.scripps.edu/. See also: N. Jones, *Nature*, 2012, **487**, 22–23.
5 The PyMOL Molecular Graphics System, Version 1.5.0.4 Schrödinger, LLC. Freely available from: www.pymol.org.
6 It should be noted that other 3D printing file formats (e.g. .STL) can be used if colour models are not required. There is much instructional value in monochromatic models as well, since they can be printed quickly and inexpensively on many of the hobbyist 3D printers that use ABS plastics as the substrate. Full colour 3D printers are still prohibitively expensive (and large) for individual use, and are thus typically house in commercial and academic facilities.
7 Y. Li and A. H. Flood, *Angew. Chem. Int. Ed.*, 2008, **47**, 2649–2652.
8 S. Lee, C.-H. Chen and A. H. Flood, *Nat. Chem.*, 2013, **5**, 704–710.
9 Freely available for Linux, MacOSX and Windows operating systems, from: http://www.ccdc.cam.ac.uk/Solutions/CSDSystem/Pages/Mercury.aspx. Last accessed on February 11, 2014.
10 Blender is free software, available for Linux, MacOSX and Windows operating systems at: http://www.blender.org/download/. Last accessed on February 11, 2014. Blender is convenient to use because of the wealth of user documentation freely available online, which is further complemented by numerous YouTube videos illustrating individual features. This body of helpful information should make troubleshooting easier for the users of our procedure.
11 Freely available at: http://epmv.scripps.edu/download-install-free/installers/. ePMV is available for Linux, MacOSX and Windows operating systems. Last accessed on February 11, 2014. Note that—at the time of this writing—ePMV operates on Blender 2.62, which is not the same as the latest version of the program (Blender 2.69 for Windows and Blender 2.70 for MacOSX). Therefore, both versions of Blender should be downloaded and used, which is fortunately possible. It is reasonable to assume that these functionalities will eventually be combined in a single version of the program, which would simplify our procedure. See also: G. T. Johnson, L. Autin, D. S. Goodsell, M. F. Sanner and A. J. Olson *Structure*, 2011, **19**, 293–303.
13 http://www.shapeways.com
14 Material Safety Data Sheet (MSDS) for *Full Color Sandstone* can be found at: http://www.shapeways.com/rrstatic/material_docs/m-sds-sandstone.pdf.
15 For comparison, building a model of a single unit cell of MOFF-3 using modular commercial molecular model kits would cost approx. $300. In addition, these sizes of atoms in these kits are too large to make them practical for MOF structures with numerous atoms; thus, a single unit cell model for MOFF-3 would be 30 × 30 × 30 cm large. 3D Printed models permit much smaller feature sizes.

Graphical Abstract



Author Biographies

Teng-Hao Chen *received a BS degree in Chemistry from National Taiwan University in 2006. After graduation, he worked as a research assistant in the Industrial Technology Research Institute in Hsinchu, Taiwan for one year. He is currently pursuing a PhD in Chemistry at the University of Houston in Prof. Ognjen Miljanić's group. His research focuses on the synthesis and applications of novel porous materials.*

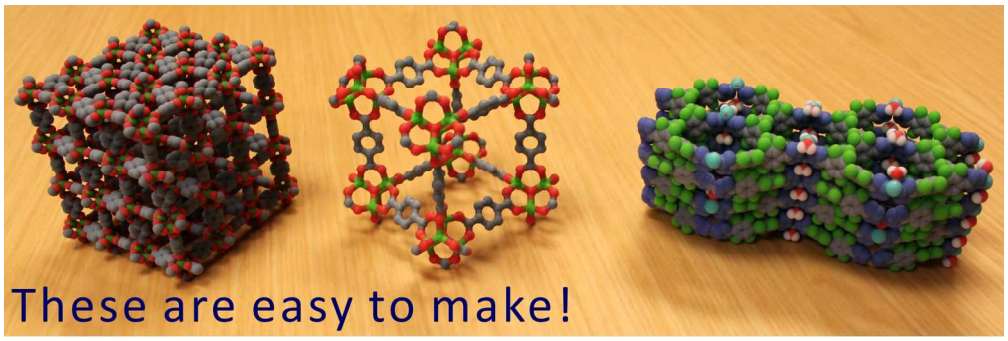


Semin Lee *received his BS (2006) and MS (2008) degrees at Sogang University, South Korea, under the supervision of Bongjin Moon. In fall 2009, he joined the Professor Amar Flood's laboratory at Indiana University as a PhD student. His research is focused on designing new anion receptor molecules, such as cyanostars, and investigating their materials properties.*

Amar H. Flood *was born in New Zealand where he received his BSc (Hons) and PhD (2001) from Otago University with Keith C Gordon. During his postdoctoral studies at UCLA with Fraser Stoddart, his appreciation for visual representations of chemistry grew. In 2005, he started as an Assistant Professor at Indiana University and in 2009 printed his first molecular models in 3D. He is a Camille Dreyfus Teacher-Scholar and the James Jackson Associate Professor of Chemistry. He is the recipient of a NSF CAREER Award, Cram Lehn Pedersen Prize and the Award for Early Excellence in Physical Organic*

Chemistry. His research interests are anion recognition, molecular switches and surface self-assembly.

Ognjen Š. Miljanić *was born in Belgrade, then Yugoslavia, in 1978. He holds a Diploma (2000) from the University of Belgrade and a PhD (2005, with Peter Vollhardt) from UC Berkeley. In 2008, following a postdoctoral stay at UCLA with Fraser Stoddart, Ognjen started his independent career as an Assistant Professor at the University of Houston. He is the recipient of the 2012 NSF CAREER and 2013 Cottrell Scholar awards. His research interests include dynamic combinatorial libraries and metal-organic frameworks.*



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