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Three-Dimensional Printing of Ellipsoidal Structures Using Mercury: Electronic Supplementary Material

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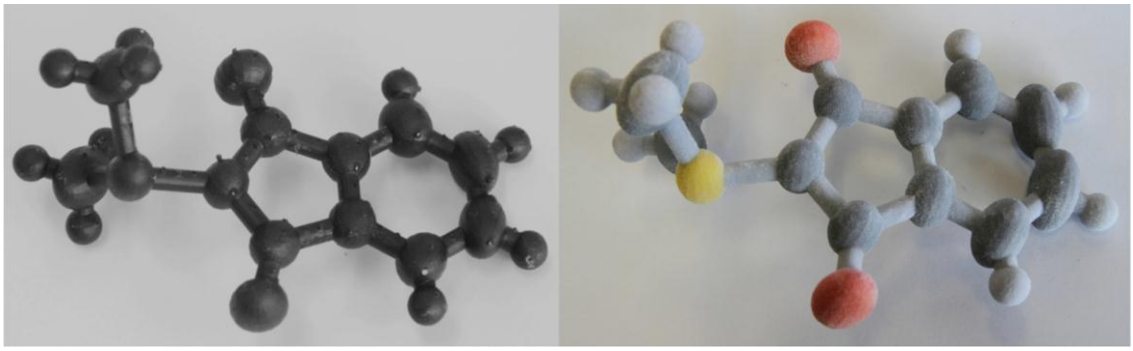
Equipment: Coloured structures were printed on either a ZPrinter 450 or 650 from ZCorporation. All monochrome parts were printed using either a Formlabs2 SLA printer or a Fortus 250mc printer.

Software: Ellipsoidal structures were generated using Mercury 3.9 (Build RC1) or earlier and the 3D print files were saved in VRML (WRL) format. Files printed in monochrome were converted from WRL files to STL files using the Zprint software. Ball and stick and space filling structures were generated from crystallographic information using either Mercury or and Chimera (As described previously.[2b] The watertightening steps were done using Materialize Magics (19.01, 64-bit) while Formlabs Preform or Fortus Insight were used for the printing monochrome structures.

Origin of Structures. All crystallographic information files were generated from data collected at Simon Fraser University. The original publications for these structures are provided in citations 6–8.

Mercury Procedure for Ellipsoidal Structures Printed:

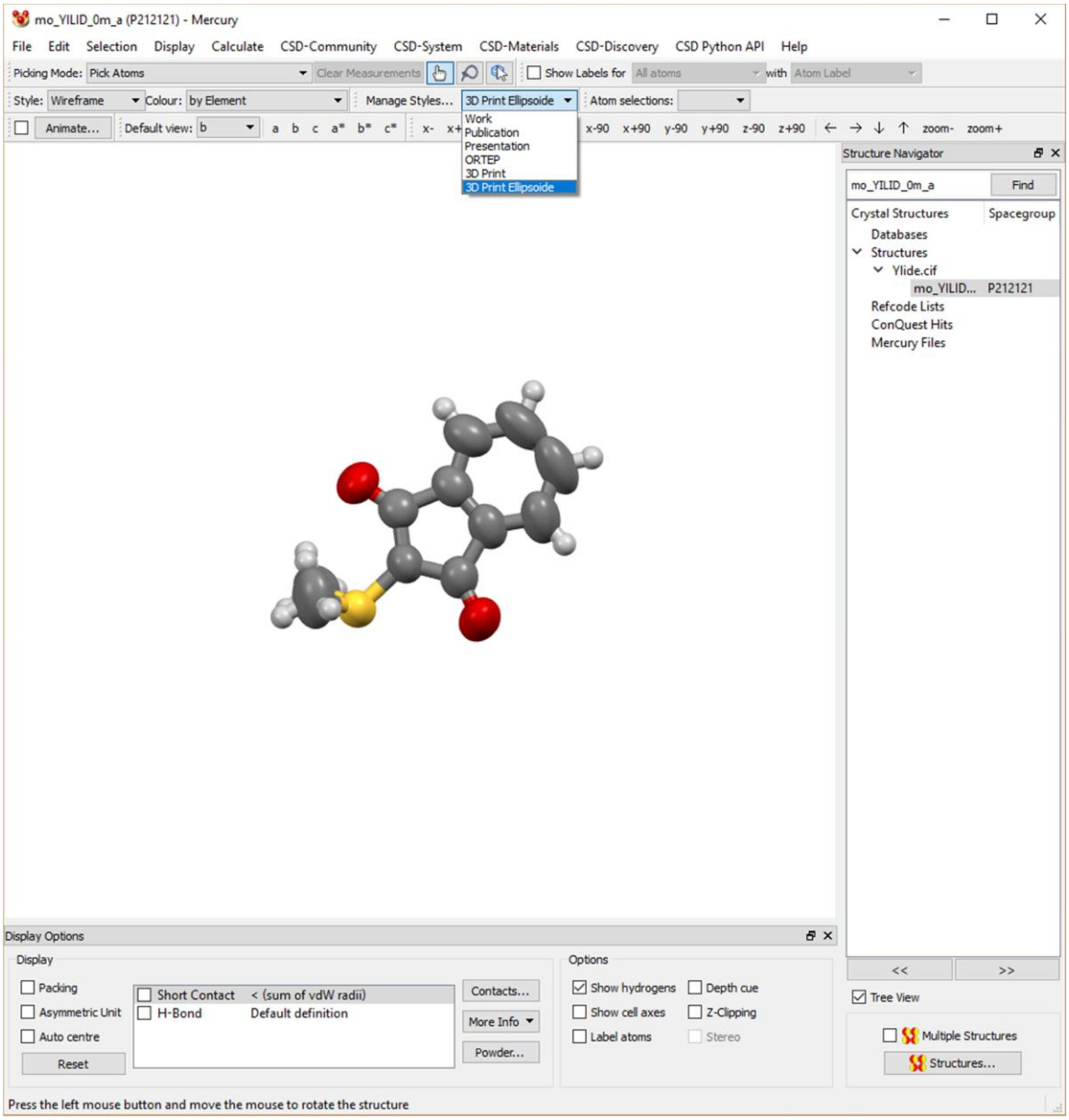
An example structure is shown in Figure S-1, and this molecule is used to demonstrate the steps to print a 3D model of an ellipsoidal representation.



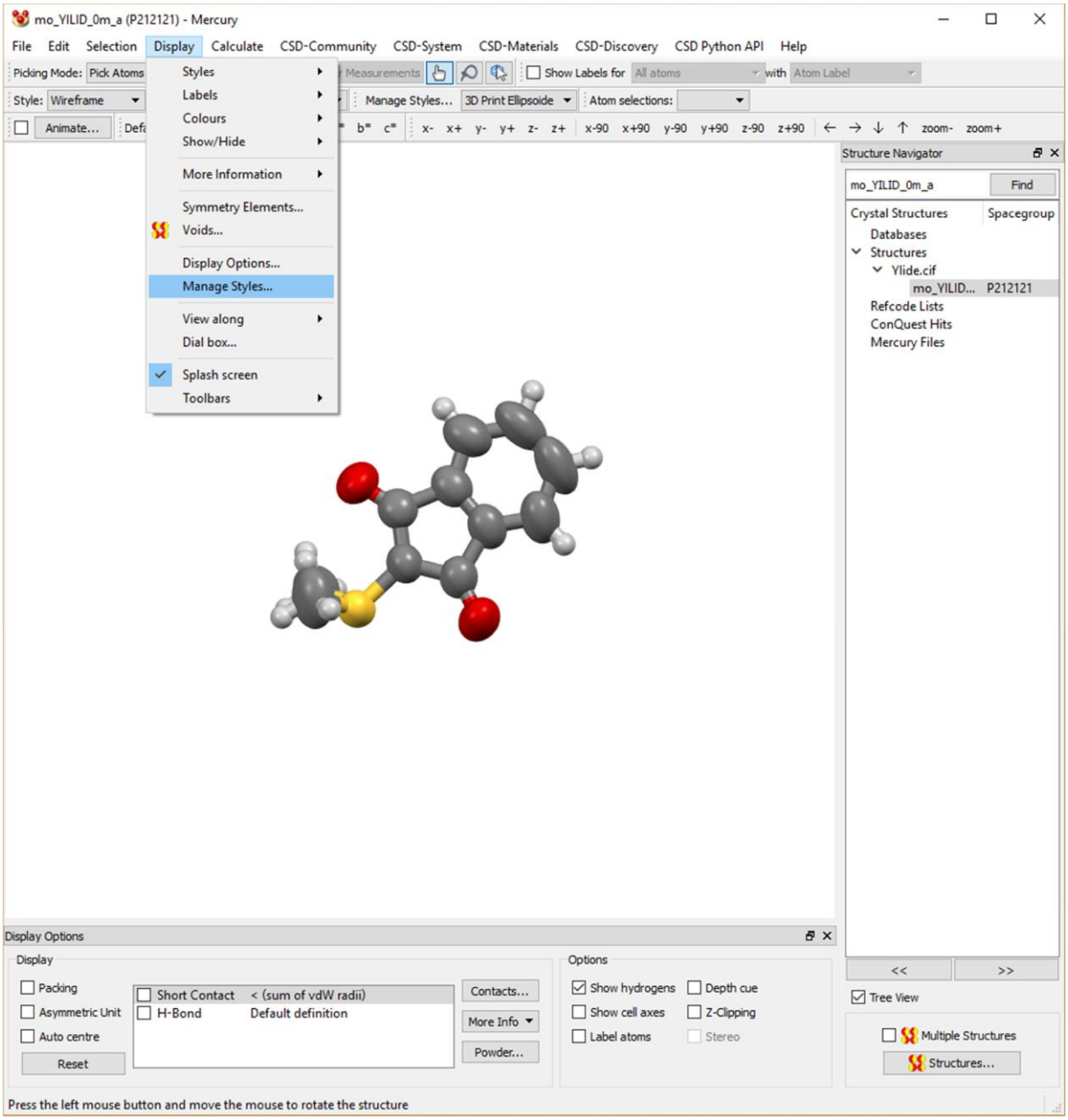
S-1: 2-Dimethylsulfuranylidene-1,3-indanedione[5] (Ylid) Ellipsoidal models. Printed on a ZPrinter 450 from ZCorporation (Left) and Formlabs2 SLA printer (Right). Note that the much smaller Formlabs2 model shows the ribbing less than the large model from the ZPrinter.

The first step to printing an ellipsoidal model is to prepare the relevant structure or structural fragment in Mercury (Figure S-2). A crystallographic information file (CIF) that includes anisotropic displacement parameters is needed. Currently the abbreviated files deposited with the Cambridge Structural Database (CSD) or the Inorganic Crystal Structure Database (ICSD) lacked the anisotropic displacement parameters. However, the Cambridge Crystallographic Data Centre (CCDC) has announced that starting in 2018 the CSD will include anisotropic displacement parameters with select structures.[5]

Once the selected file is verified to contain anisotropic displacement parameters it must be made suitable for three-dimensional printing. To start with this means that the object to be printed must be completely connected: if two halves of a non-coordinated salt are to be printed, for example, it is recommended that they be saved as two separate files and printed separately. The easiest way to do this is to either delete or hide the unwanted atoms in Mercury. The colours of the atoms to be printed should be set and any unwanted bonds caused by close contact should be removed. Additionally, any hydrogen or coordination bond that is not automatically present in the structure should be added at this time.



S-2. Loaded Ylid structure ready to be manipulated in Mercury. The *Select Styles* menu is shown. Once you have your styles set up, this can be used to quickly switch between them. The *Manage Styles* button to the left of the menu is an alternate method of opening the *Manage Styles* window (Shown in Figure S-3)

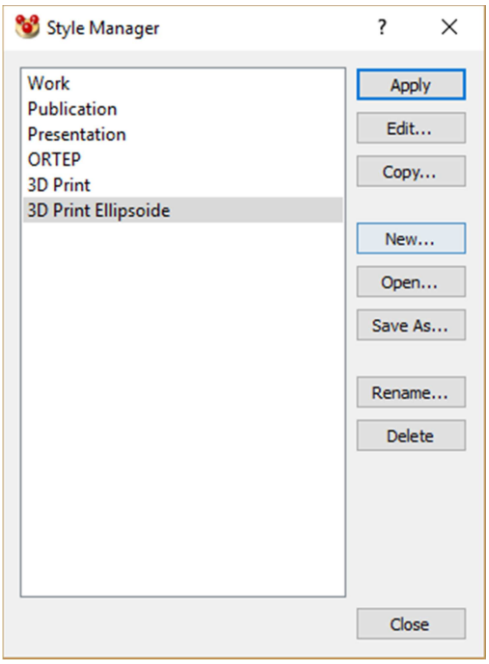


S-3. Opening the *Manage Styles* dialog via the *Display* menu.

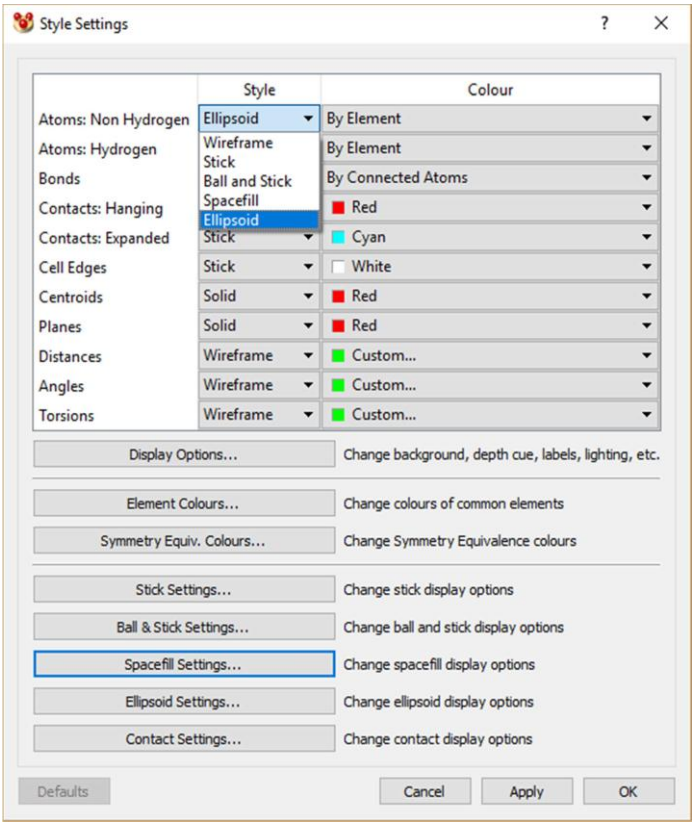
The next step is to go into the *Manage Styles* drop down menu (Figure S-2) and select *3D Print* which sets many of the default options to be closer to what a 3D printer is actually capable of constructing.

Now open the style manager via going to *display* → *manage styles* (Figure S-3). It is recommended (but not required) to copy the *3D print* style into a new entry such as "3D Print Ellipsoid" so as to

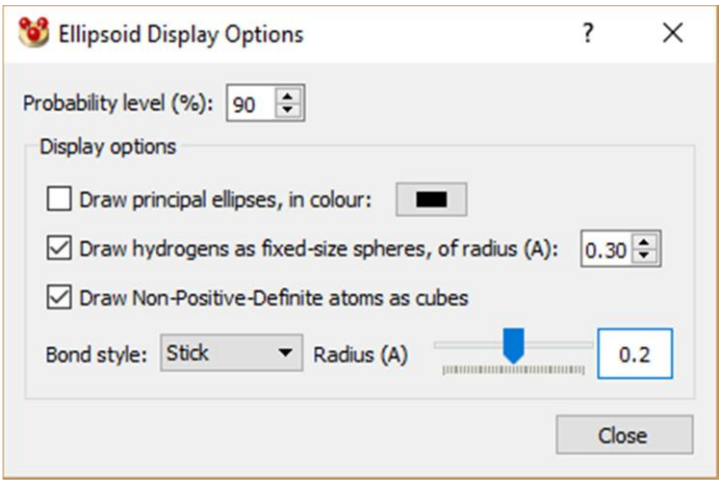
always have a backup of the default Mercury settings. (Figure S-4) The next step is to select the newly created style, apply it, and then press the edit button on the right-hand side. At the top there is a list of features for which the settings can be altered, while below there is a series of buttons that will open further settings. The first thing to do is at the top change *atoms: non-hydrogen* from *ball and stick* to *ellipsoid* (Figure S-5). Then go into *ellipsoid settings* at the bottom and alter the probability level until the atoms are of the sufficient size to distinguish them clearly from the connecting bonds. The optimal setting has been found to typically be between 90 and 99% (Figure S-6).



S-4. Mercury Style Manager window.



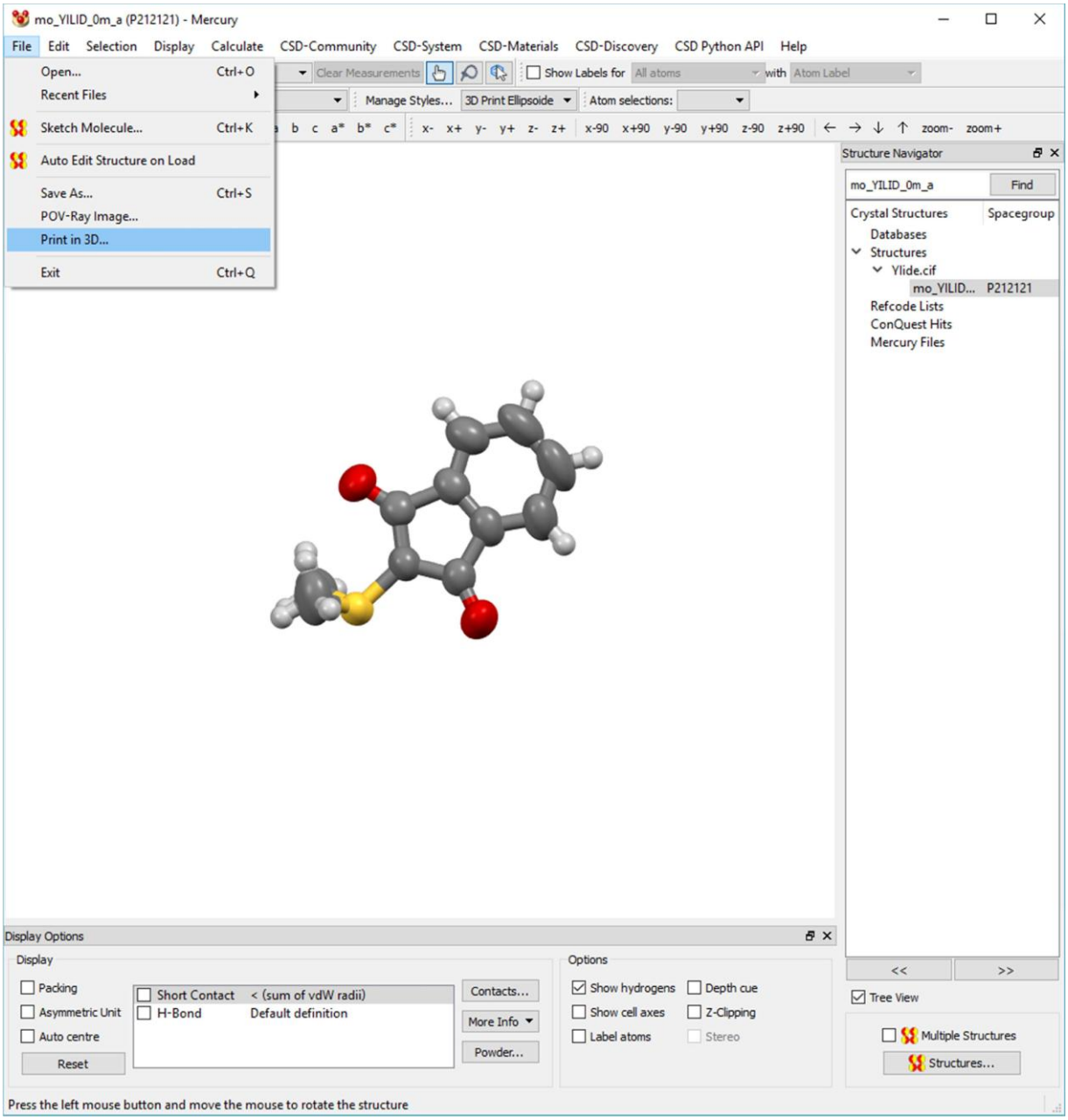
S-5. Mercury Style Settings window.



S-6. Mercury Ellipsoid Display Options window shown with sample settings.

It is also common to have to alter the radius of the hydrogen atoms to aesthetically match the size of the non-hydrogen atoms. In the structures shown within this paper a value of 0.30–0.35 Å was used. (Figure S-6) As hydrogens are spherical, they were used to determine the scale of the rest of

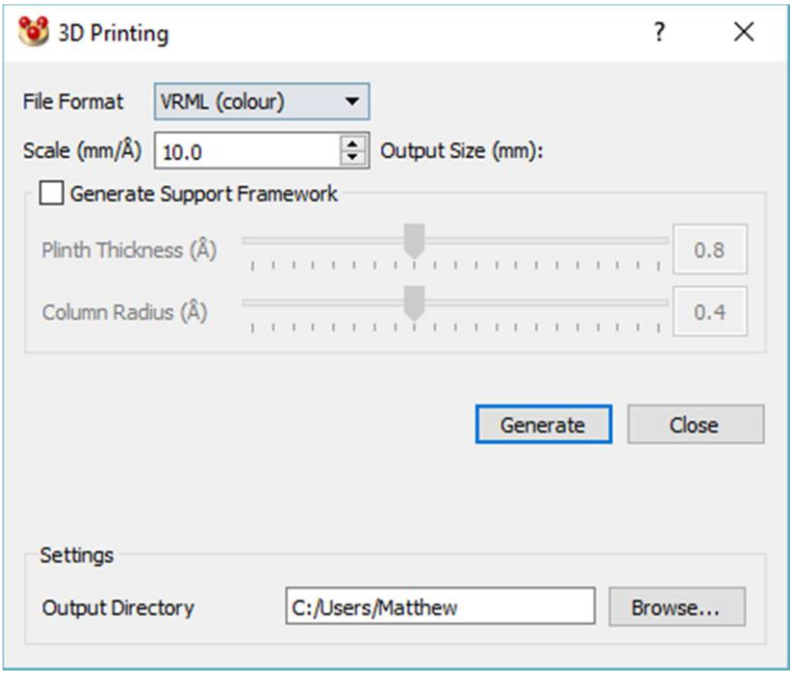
the model in the 3D printer's proprietary software, as the printer software was able to easily measure the real post-printing size of the spheres. This was used to estimate if the bonds were thick enough to support the structure. Based on these measurements, the thickness of the bonds may need to be increased. A value between 0.15 and 0.35 Å was used in the preparation of the models for this paper, though the exact thickness used will depend on the material used for printing, the size of the ellipsoids that need to be supported as well as the number and length of the supporting bonds. Once the bond thickness is set the size of the ellipse may have to be adjusted so that the atoms are not hidden inside the connecting bonds. This is a balancing act and some experimentation will be required to see what the optimal mass of spheres versus thickness of bond ratio, since a thicker bond can support a heavier weight, but that in turn requires a larger atom to be seen around the connecting bond. The settings can be previewed at any time by clicking *close* at the bottom of the ellipsoid settings window and pressing *apply* at the bottom of the style settings window.



S-7. Opening the *Print in 3D* dialog.

Once the structure was deemed satisfactory for a trial print, the operation print in 3D was selected in the File menu (Figure S-7). Two file formats are available: *VRML* (Virtual Reality Modeling Language, also labelled WRL) that will allow color printing and *STL* (STereoLithography) for monochrome printing (Figure S-8). In all cases in this paper VRML files were generated. When monochrome structures were printed, the STL files used were created from the VRML files using the Zprint software. There is an option to generate a support framework. This was not used in the

generation of any files in this paper rather relying on the support framework generated by the printer specific software was used. The scale millimeters per angstrom scale setting was found to be inconsequential, since the printed object was rescaled to the specific printer box in the printer manufacturer's specific software. The resulting file can then be imported into any printer specific software and examined for flaws.

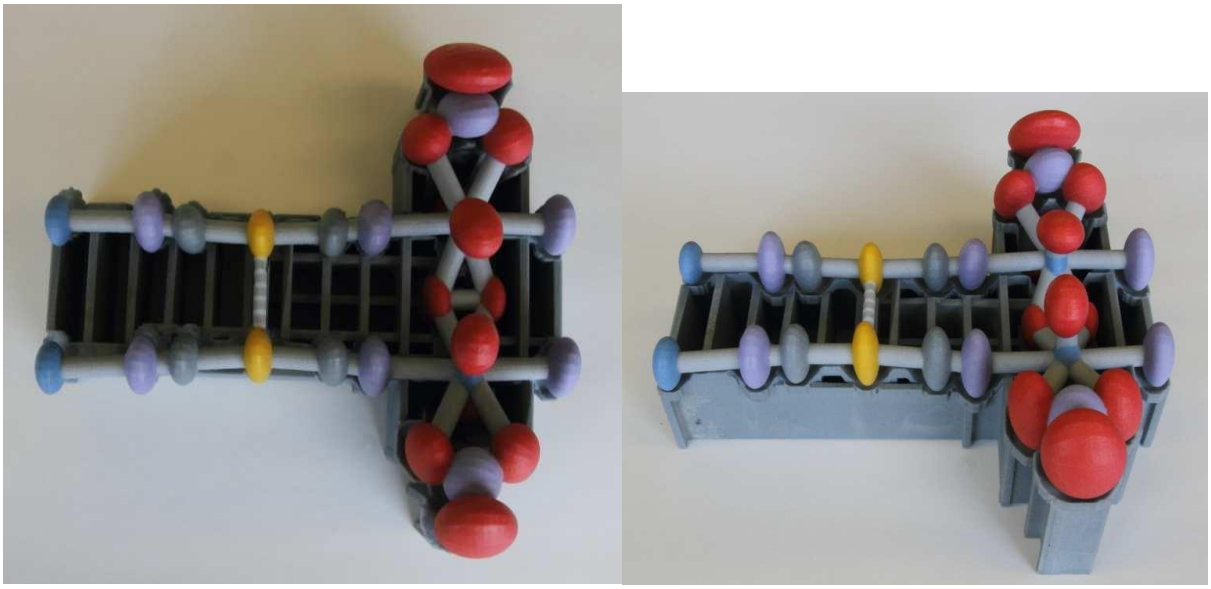


S-8. The 3D Printing dialog box. Note that Generate does not close this dialog. Therefore it can be left open as the needed settings in the style dialog are iterated upon. Also, pressing generate more than once creates files with an incremental number appended.

Cautions and warnings when using the Mercury software.

Mercury is a very powerful program capable of extending the structure based on polymer expansion, short contacts, hydrogen bonding or symmetry. However, in some cases when the structure is expended, the resulting file contains non-physical, and thus non-printable, elements such as two ellipsoids occupying the same location. Therefore it is recommended that the simplest possible fragment should be saved into a 3D printing file and the complex extended structure be saved in a separate file. That way if there are difficult to solve problems the simpler fragment can be expanded in the printer specific software into the full more complex form using the non-printable version as a guide. No difficulty was encountered in the use of dashed coordination bonds, which printed as a series of connected white and blue cylinders.

There is a small downside to printing ellipsoidal structures using Mercury. Imperfections in the ellipsoids will be visible at larger print sizes, as seen in Figure S-1,S-9 and S-26. While the ellipsoids are shown to be smooth on screen, when converted to a printable file these shapes are formed from multiple parts, giving them a ribbed or paneled look. This is present in the generated file, and is not a result of the printer in use. This can be seen when comparing Figure S-9 (printed on the ZPrinter) with Figure S-26 (printed on the Forteus), and the effect can be seen in S-16, prior to printing the structure. This downside is considered to be minor compared to the advantages of printing in this manner, and it is hoped that future versions of Mercury will correct this. As can be seen when comparing the models in Figure S-1, this effect is less visible when printing at smaller sizes.

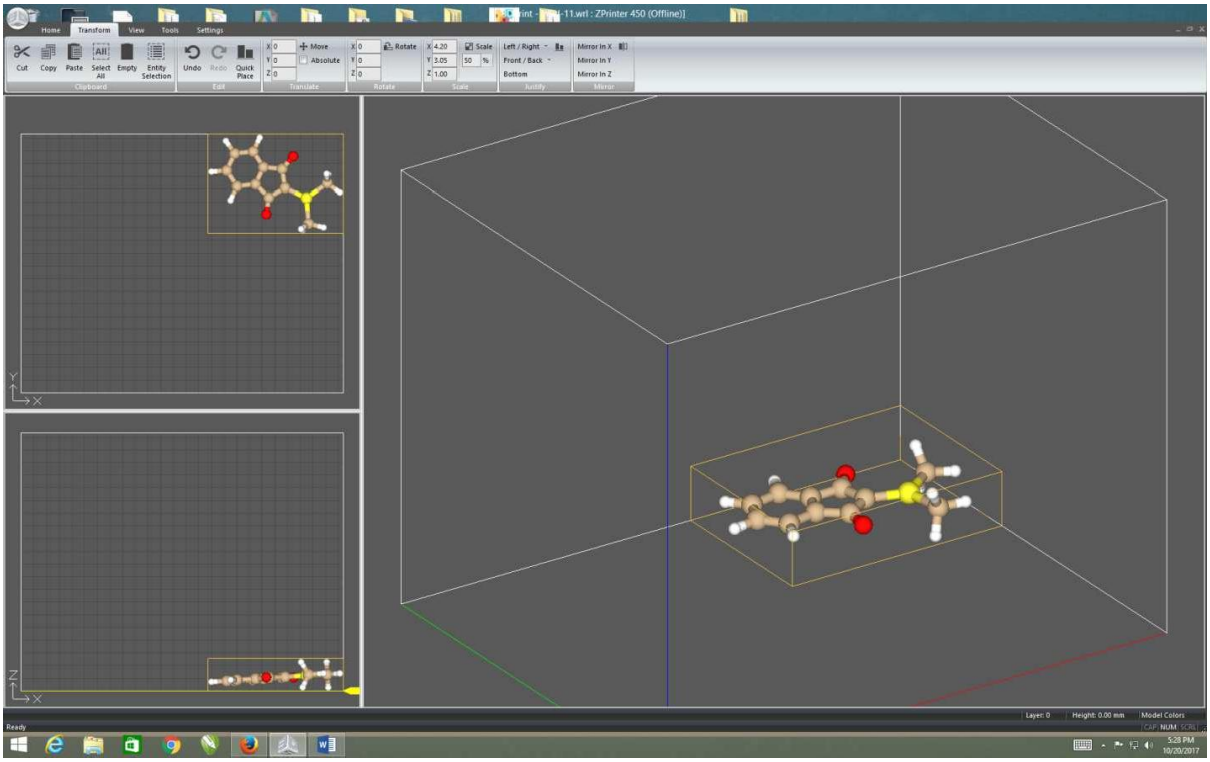


S-9. Printed Uranyl Peroxo Dicyanoaurate Coordination polymer showing the ribbing resulting from Mercury's approximation of an ellpsoid. Structure printed on a ZPrinter 650 from ZCorporation.

Procedure for Ball and Stick and Space Filling Prints

S-10. Printed structure of 2-Dimethylsulfuranylidene-1,3-indanedione as Ellipsodal (top) Ball and Stick (middle), and Space filling (bottom) forms on a ZPrinter 450 from ZCorporation.

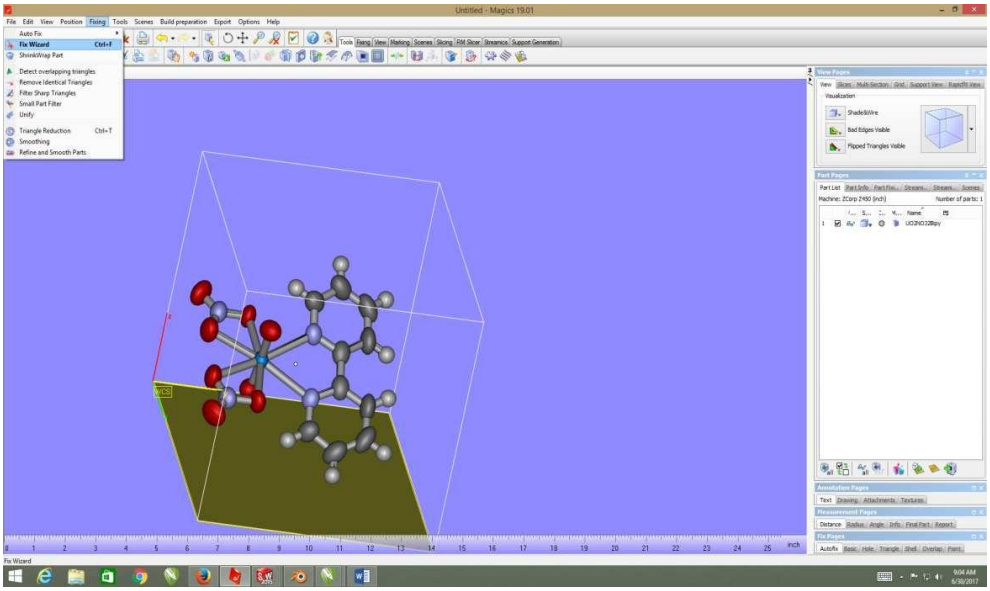
Note: Previously the technique was described[2b] using ChemDraw-Chem3D to print structures with idealized bond angles. While this is useful for pedagogy or if a crystal structure is not available, the technique described in this paper (As will that in citation 2a) will print the true solid-phase bond lengths and angles - which may be substantially different then the idealized geometry (Compare the true angels in S-1 and the naïve model in S-11)— provided the crystal structure used is correctly modeled.



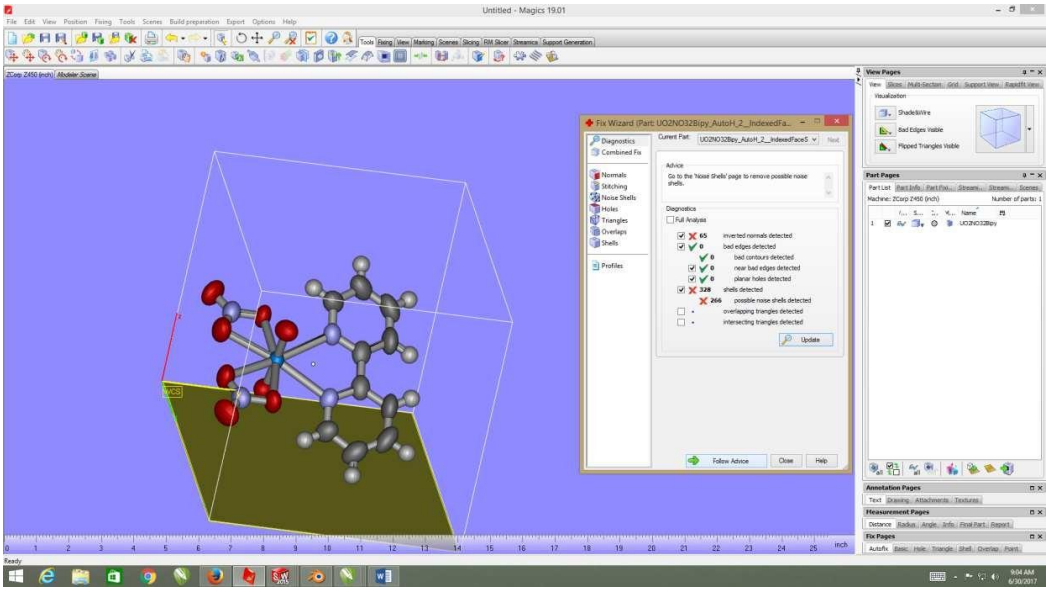
S-11. Ready to print structure of 2-Dimethylsulfuranylidene-1,3-indanedione as Ball and Stick generated from a chemdraw file.

Procedures for watertightening the structures (colored or monochrome) using Materialize Magics.

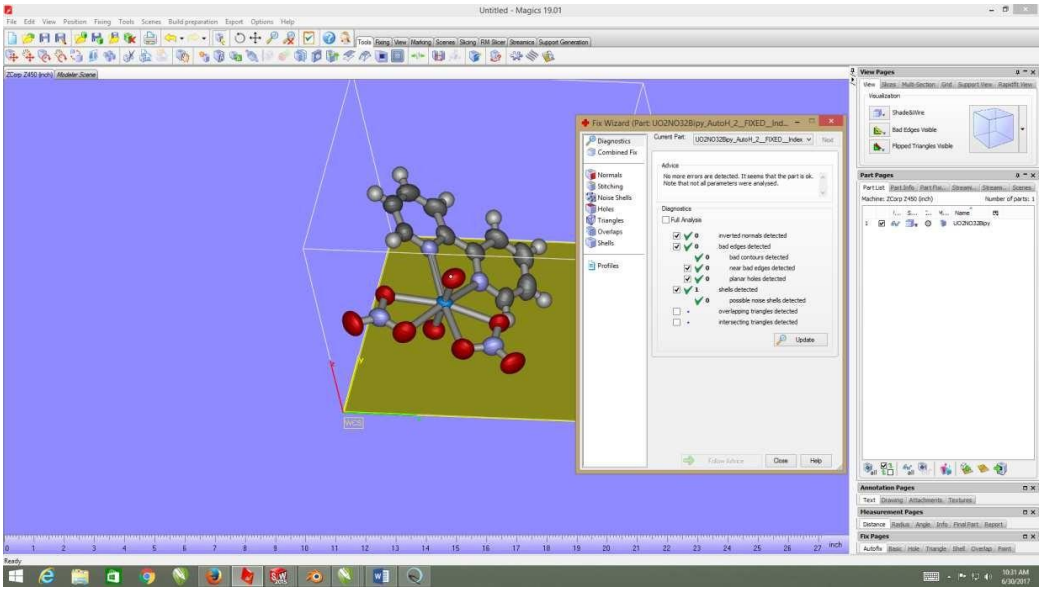
As described previously the structure file is imported into Magics and made watertight. The first step is to use the *fix wizard* command under the *FIXING* tab (Figure S-12) to make one continuous shell. Using the *fix wizard* button allows the software to find and correct any holes, bad edges, overlap triangles, etc., as seen in Figure S-13. *This step might need multiple iterations to achieve a single shell solid part without defects.* Once the part is solid use the *save part* ***as*** (stl., vrml., ply., etc…) (Figure S-14) the part is ready for printing (Figure S-15).



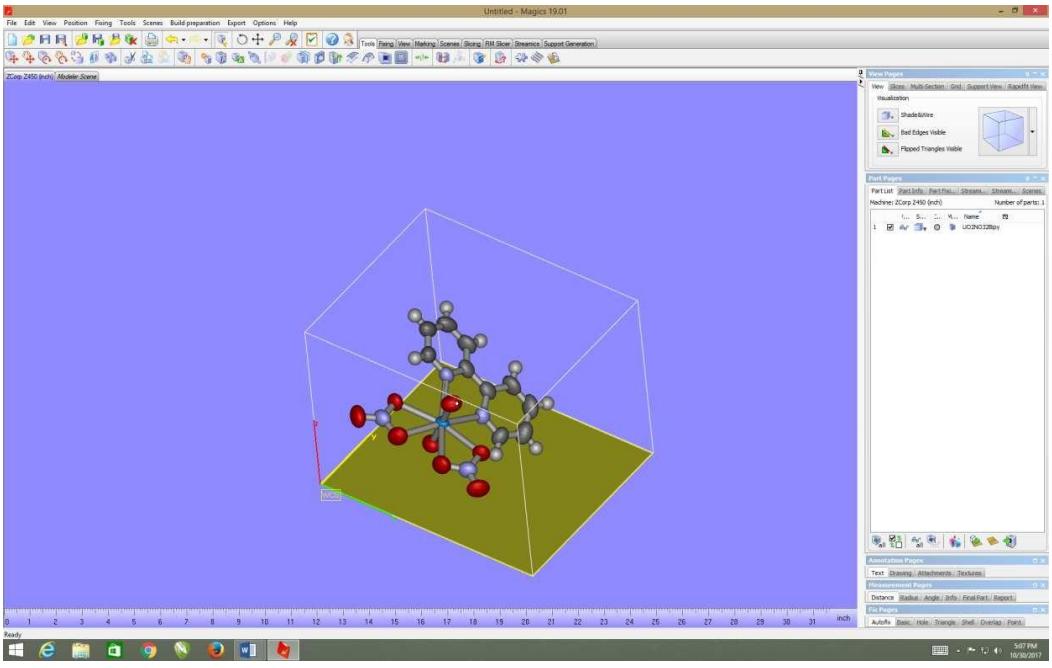
S-12. Using the *fix wizard* command under the FIXING tab to make one continuous shell of the imported structure.



S-13. List of defects that the *fix wizard* command corrects in order to unify and watertight the structure.



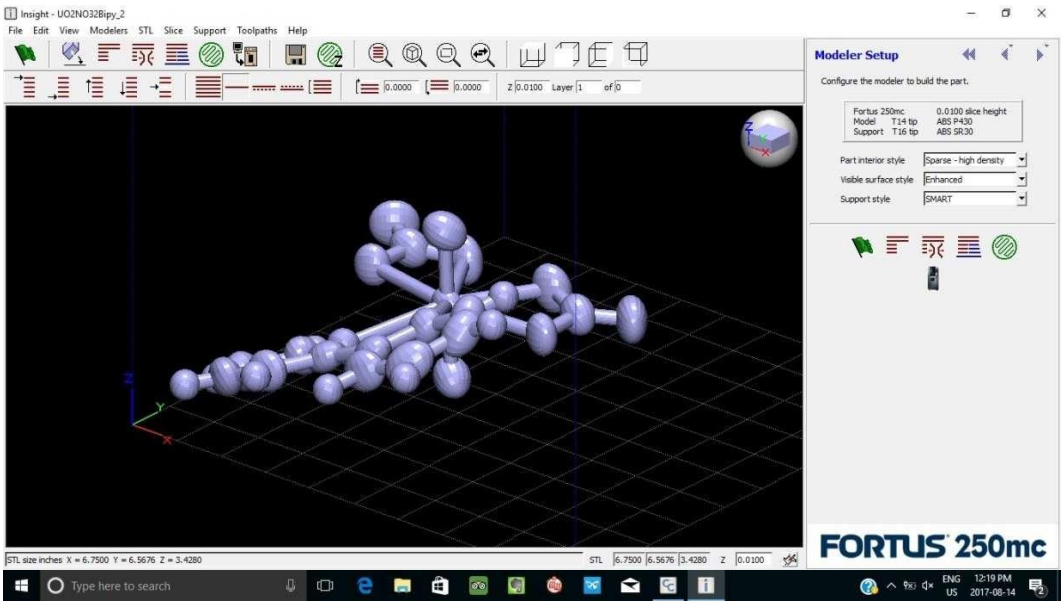
S-14. All the defects are now fixed in the fix wizard and the part is ready to be saved using *save part as* (stl., vrml., ply., etc.) the part is ready for printing.



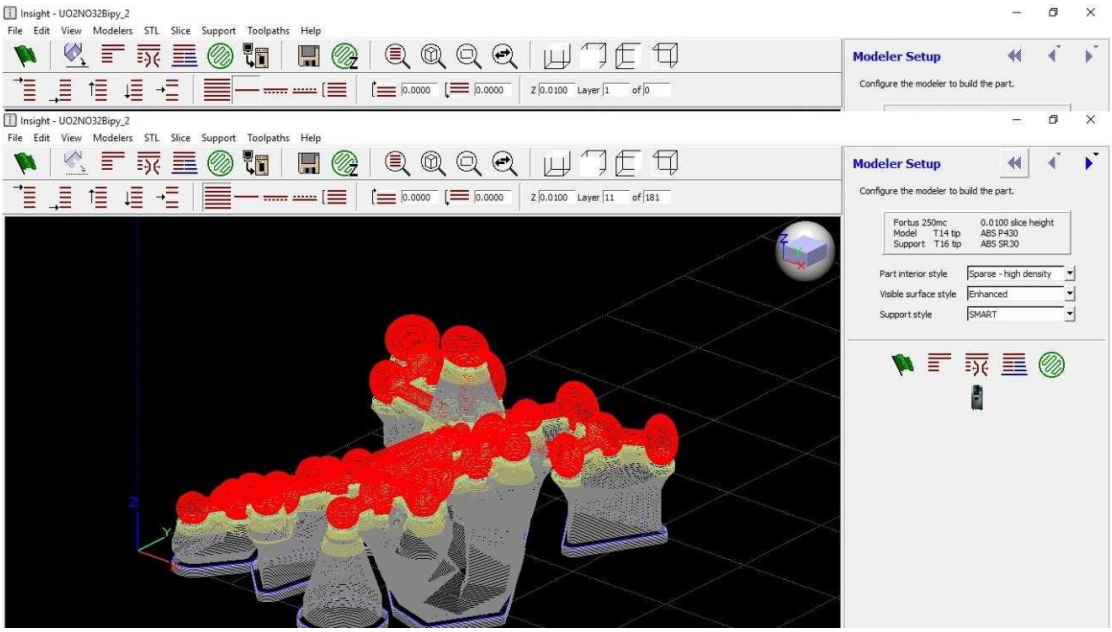
S-15. Final thermal ellipsoid structure of (2,2′-Bipyridyl)-dioxo-bis(nitrato-O,O′)-uranium watertightened and saved in the desired format using Materialize Magics.

Procedures for watertightening of the monochrome structures using Insight.

The STL file was loaded and the structure was checked with Insights pre-slice command to look for any open ends, unattached faces, or defects in the model. The model is then sliced into the printable layers (Figure S-16) and the SR-10 - P400SR Soluble Support Material is added. (Figure S-17)



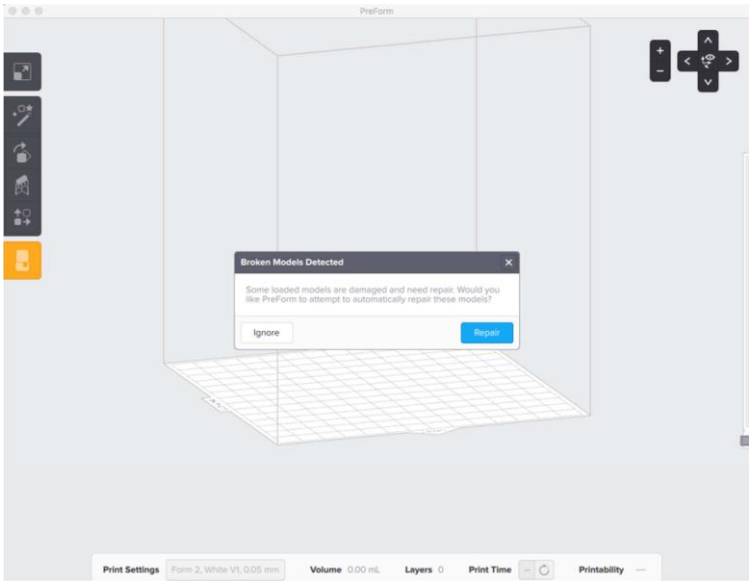
S-16. No errors found so the model is ready to be sliced into its printable layers.



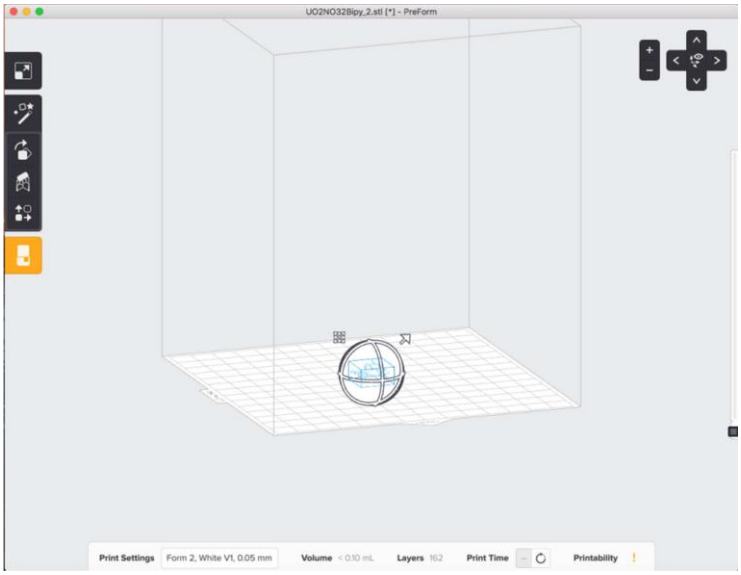
S-17. The Model shown here is ready to print. ABS Material (red) with SR-10 support (white)

Procedures for watertightening the monochrome structures using Preform.

The STL file was loaded and checked using Perform using the command *Repair* (Figure S-18), when damages are detected the software repairs them and the part is subsequently ready to be re-sized for print. (Figure S-19)



S.18. Preform is looking for any open ends or unattached faces it is also determining the break away support structure needed to print.



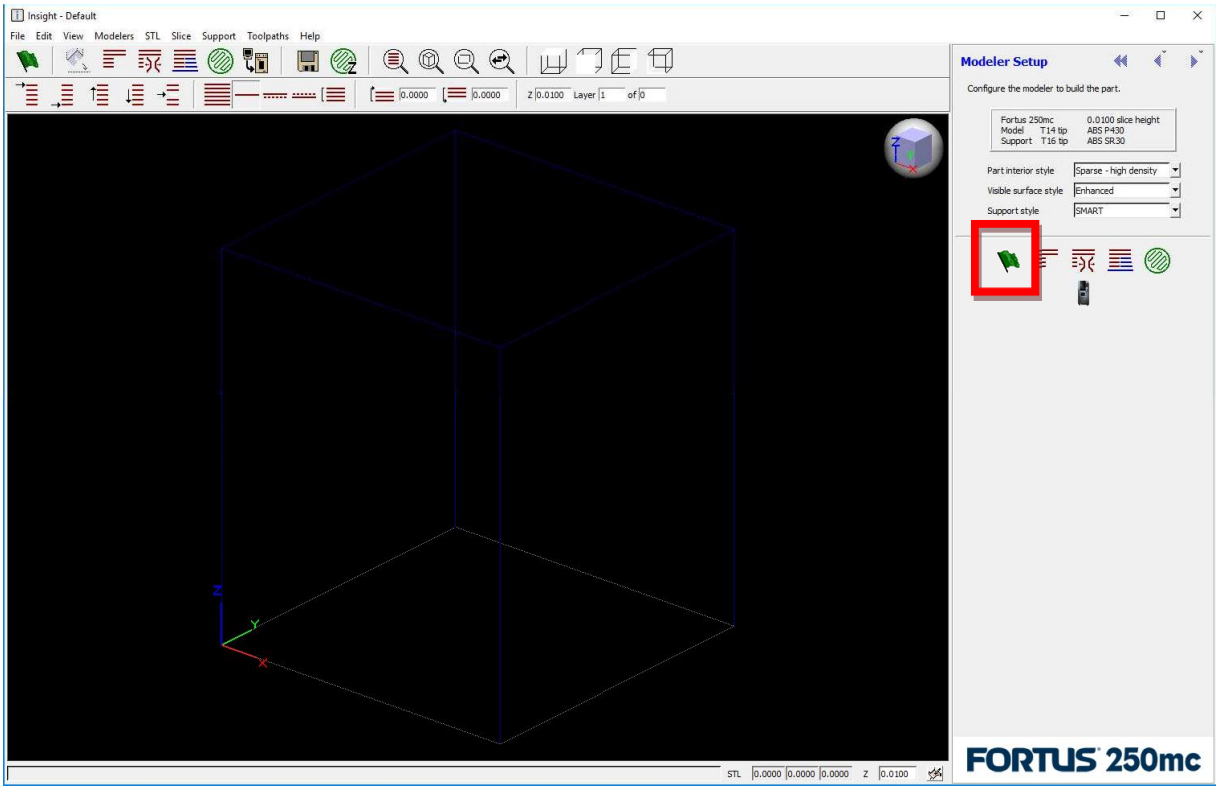
S-19. PreForm does not keep the proper size of the finished stl file, so it is scaled by hand.

Procedure for 3D printing the finished file:

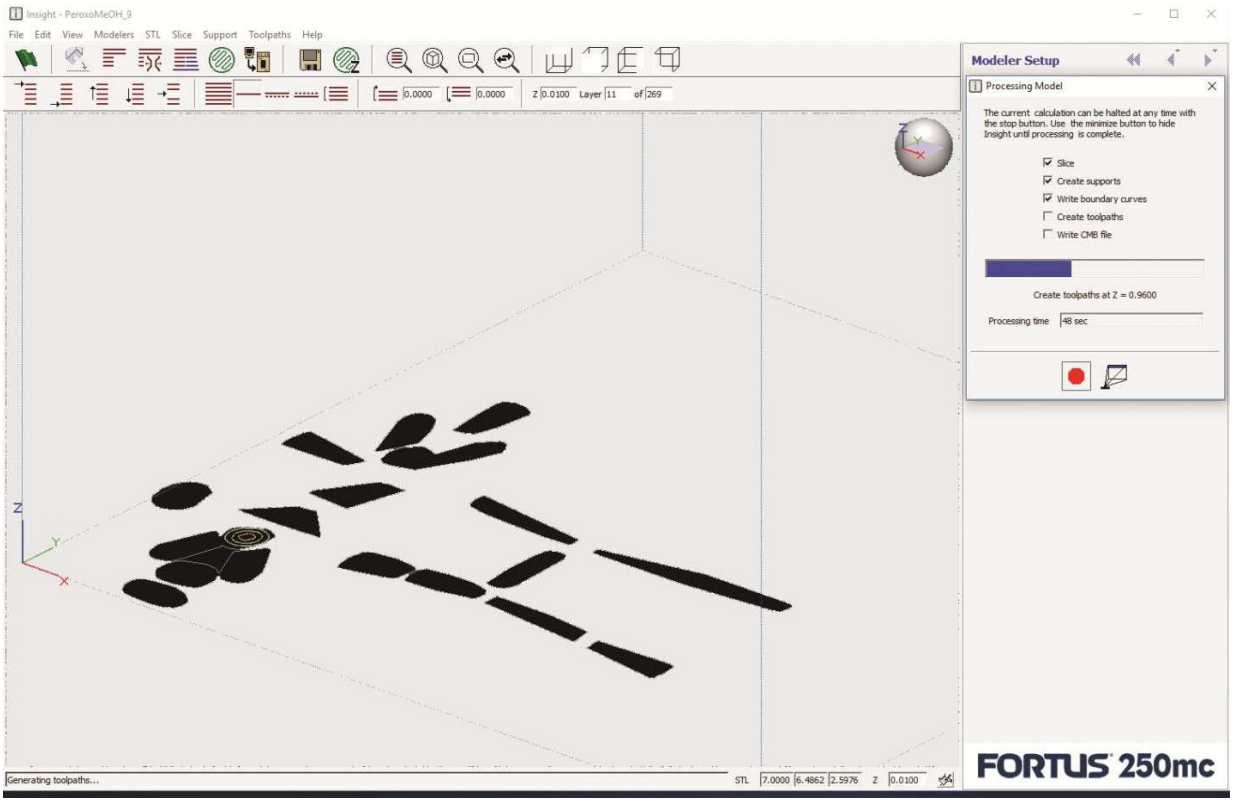
The procedure for printing these files on a ZPrinter has been previously outlined in the Electronic Supplementary Information to K. Van Wieren, H. N. Tailor, V. F. Scalfani and N. Merbouh, Rapid Access to Multicolor Three-Dimensional Printed Chemistry and Biochemistry Models Using Visualization and Three-Dimensional Printing Software Programs, *J. Chem. Educ.*, 2017, **94**, 964–969.

While the Zprint software was used to convert WRL files to STL files for printing in this case, STL files can be directly exported from Mercury. Alternatively, the gratis software Mesh Maker (http://meshmaker.com)can convert WRL files to STL files.

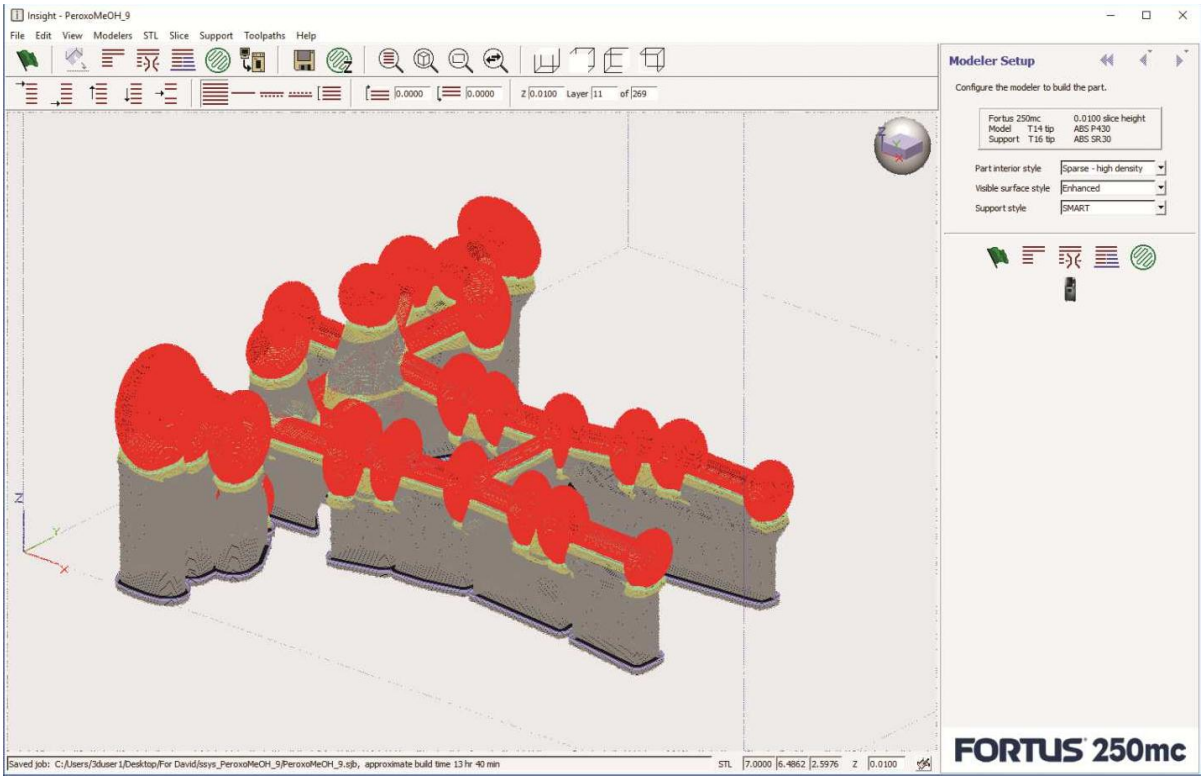
The following procedure can be used to print the file from a Fortus 250mc printer (The procedure for a Formlabs2 SLA printer is similar):



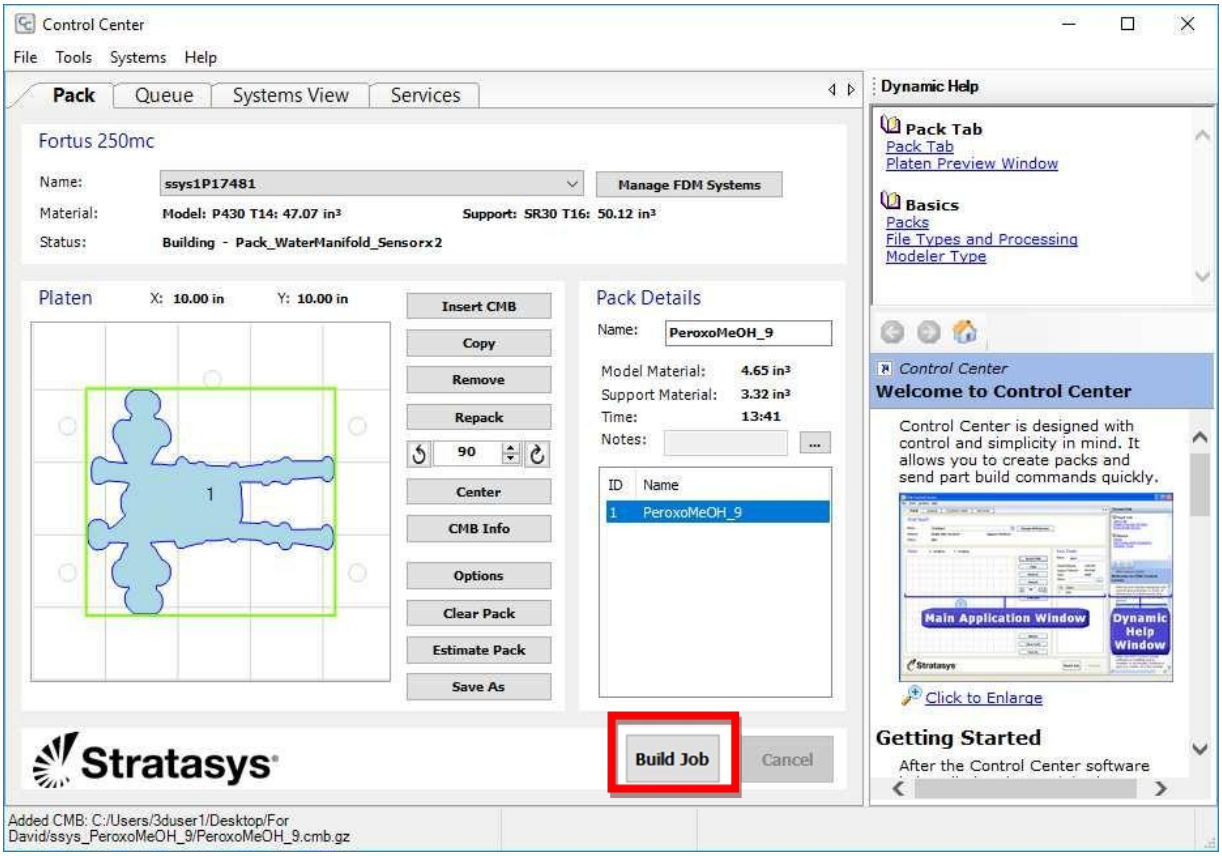
S-20: Open the file in Fortus Insight via *File* → *Open* → *Choose File* stl. Press *Green Flag* icon (Highlighted in red) to initiate the finish sequence.



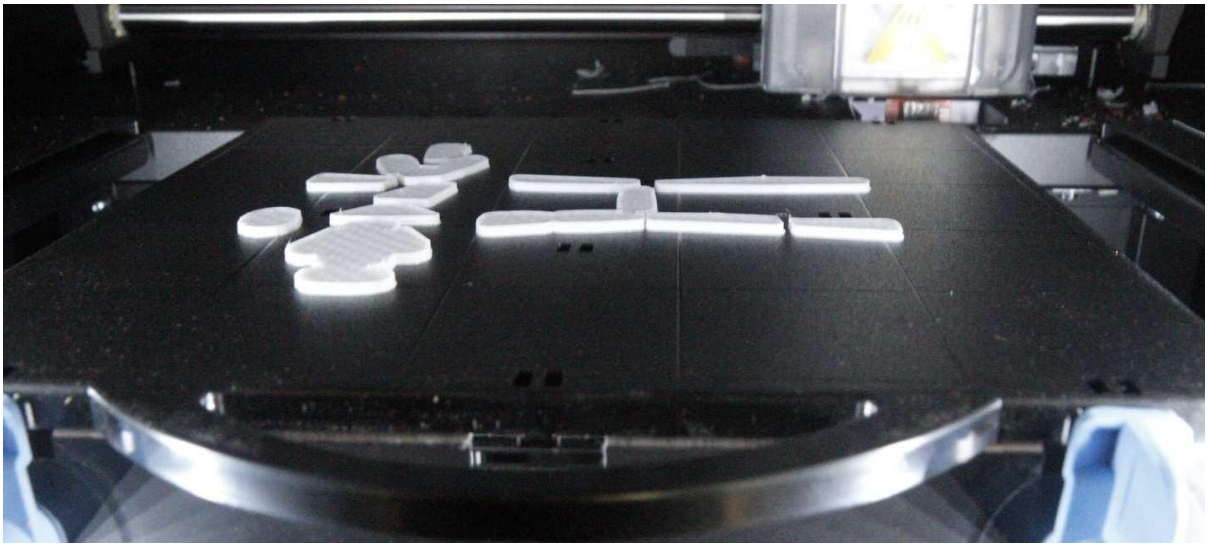
S-21: Pressing the Green Flag icon starts a set of operations that is proprietary to the printers software. The steps include: Slice, Create Supports, Write Boundary Curves, Create Tool Paths, Write CMB File (Printers File Extension).



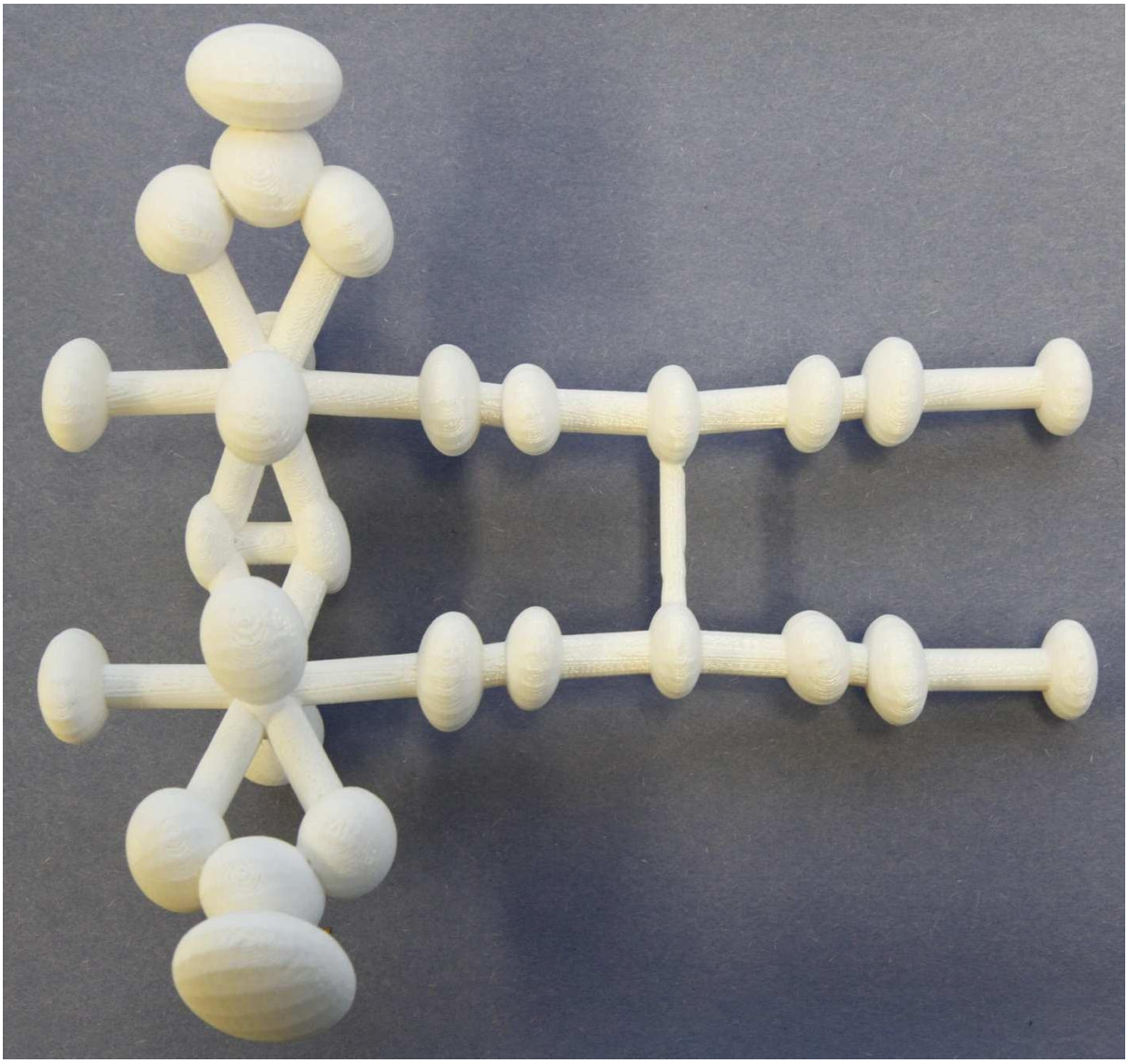
S-22: *File* → *Print* or *Print* Icon to send the part to the printer.



S-24: Press *Build Job* icon (Highlighted in red) to start the printer.



S-25: The structure in the processes of being printed.



S-26: The finished and printed structure. Note that the same paneling effect seen in the ZPrinter structures is present despite the different printer in use.