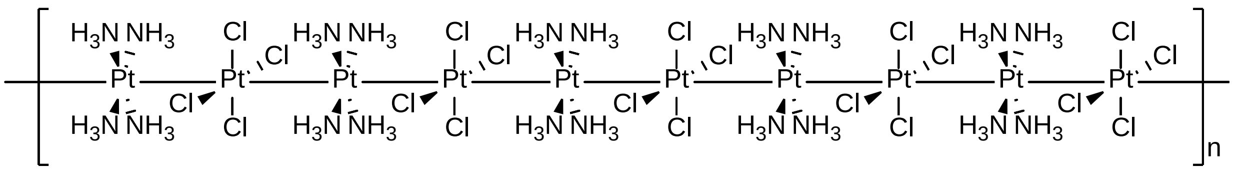
Recommended reading: **16.7-16.10** (3rd/4th edition)

Ch 102 – Problem Set 2
Due: Thursday, April 20, 2017– ***Before Class***

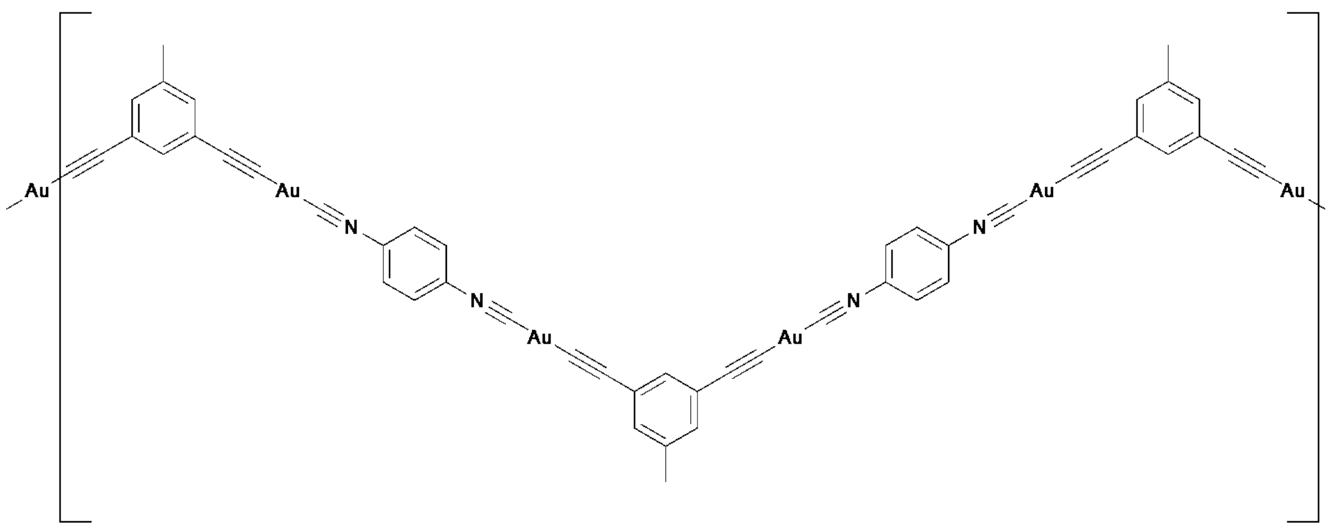
Problem 1. (3 points)

Metal-containing polymers have been studied for a wide variety of applications. For all of the complexes below, determine the 1-D symmetry class. Indicate the unit cell and asymmetric unit for each, and label the symmetry elements contained in the unit cell.

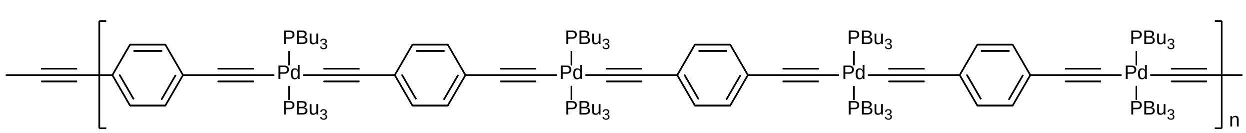
Perhaps the oldest such compound was Magnus's Green Salt discovered in the 1830's. In 1971, Gomm et al. reported anisotropic conducting properties for this compound, with high conductivity in the direction of the metal chain (Gomm et. al., *J. Chem. Soc. A*, **1971.** *2154*).



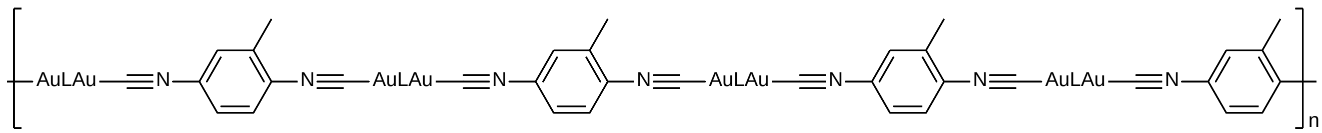
Metal-containing polymers often have rigid bidentate ligands bridging metals. Gold and platinum are commonly used in the synthesis of such materials, as shown below (Puddephatt, *Chem. Comm.* **1998.** *1055*).

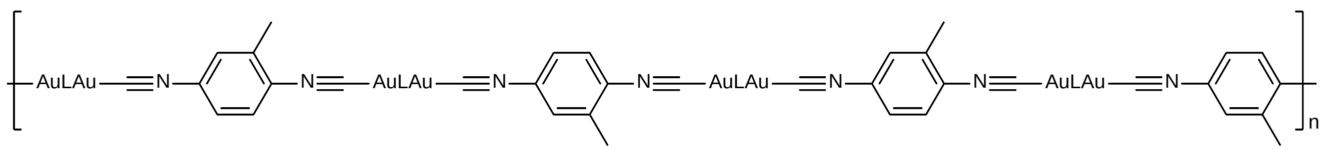


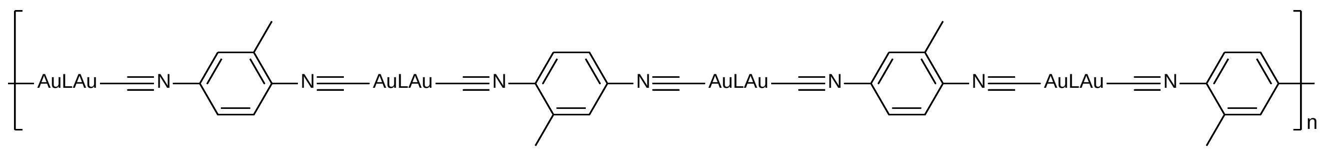
Metal-organic polymers containing π-delocalization along their entire length have been investigated for their conductive properties, as well as for nonlinear optics and crystal fluids. For example, Frazier et al. reported a large nonlinear refractive index for a palladium poly-yne (Frazier et al. *Polymer*. **1987.** *28*, 553).



Irwin et al. reported a variety of linear gold structures with a variety of linear aromatic linkers, including 1,4-diethynyl-2-methylbenzene (Irwin et al. *Organometallics*. **1996.** *15(1)*, *51*). Selective polymerization is not reported; however, several potential selective products could be envisioned, including:

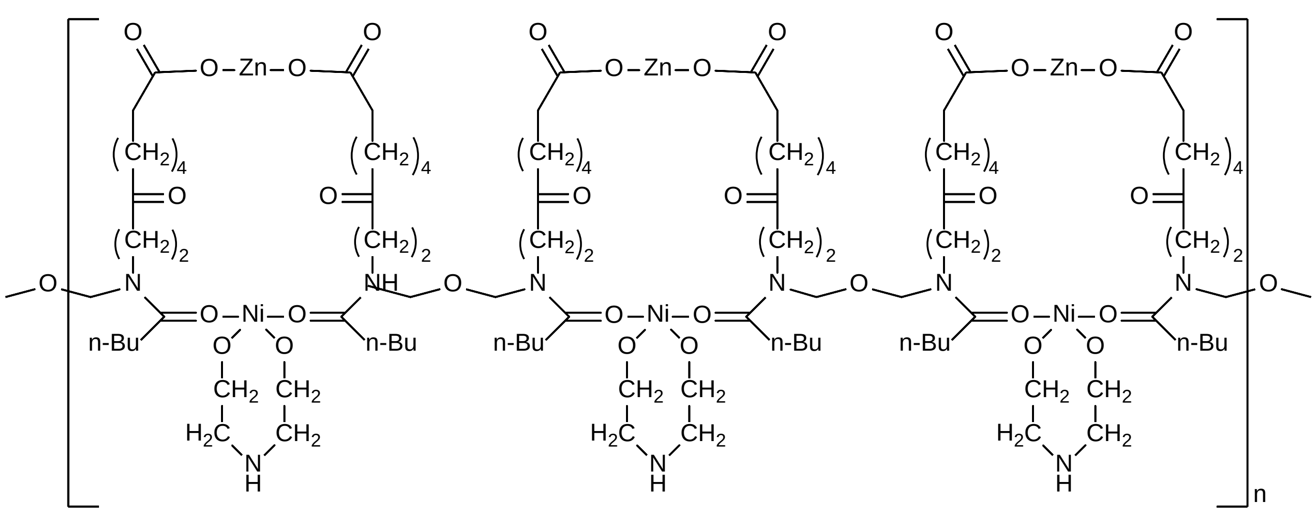




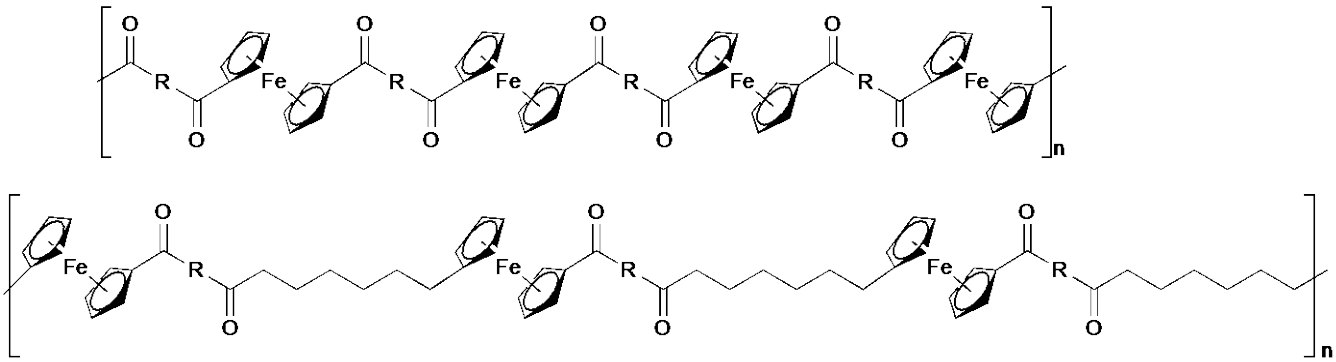


Note: Treat the "AuLAu" unit as a circular linker.

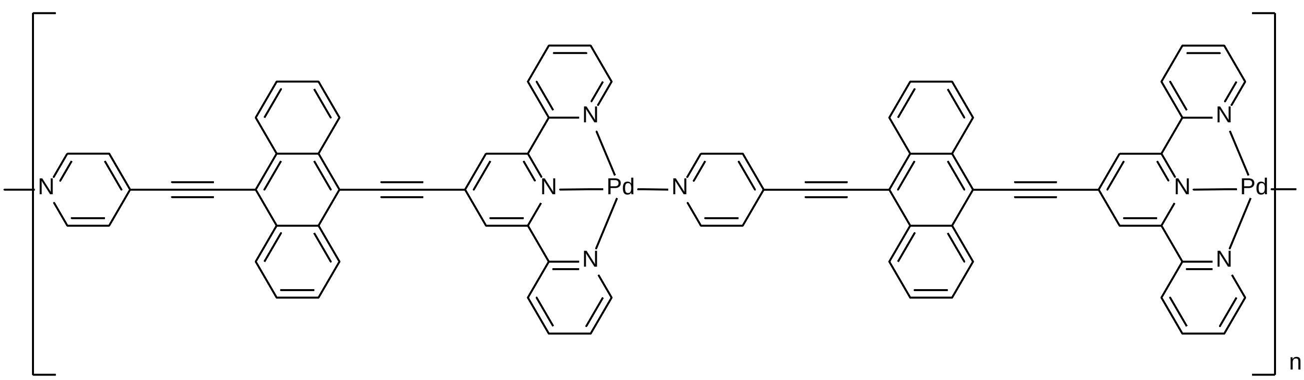
Metal-containing polymers are not only of interest for their physical properties. Many biochemically interesting metal polymers have also been investigated. For example, Singh et al. has reported a bimetallic polymer with antifungal activity (Singh et al. *Int. J. Pol. Mat. & Pol. Biomat.* **2012.** *62, 653*).



Gul et al. has reported a variety of ferrocene-based polymers with antimicrobial, antitumor, and antioxidant properties that are also DNA protecting, including those below (Gul et al. *Macromolecules*. **2013.** *46(7), 2800*). (Assume the cyclopentadienyl rings are circular).



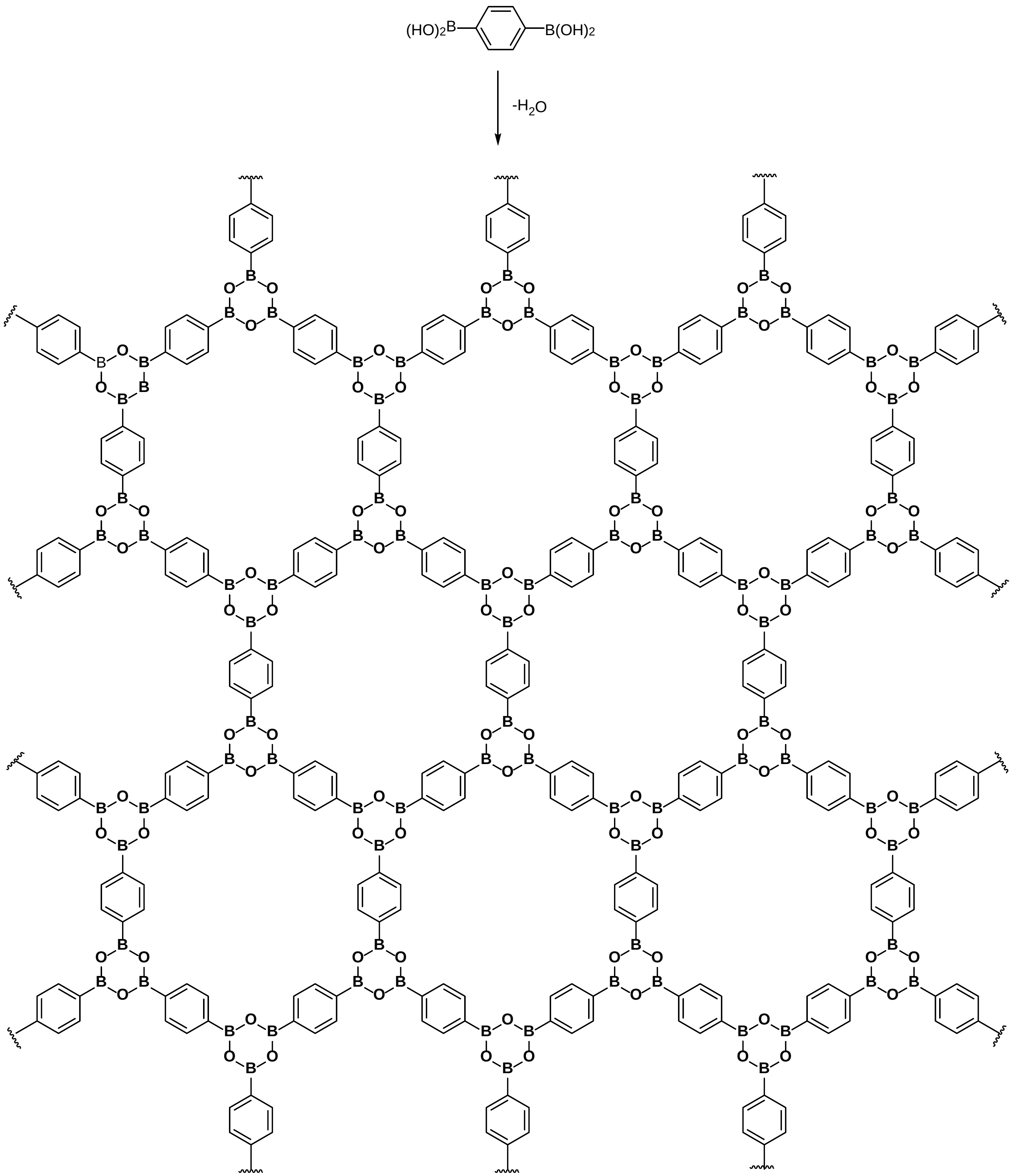
The use of metal-containing polymers are also studied with the goal of depositing them on surfaces, such as the below polymer that Surin et al. decorated graphite with (Surin et al. *Angewandte Chemie*. **2006.** *46(1-2), 245*).



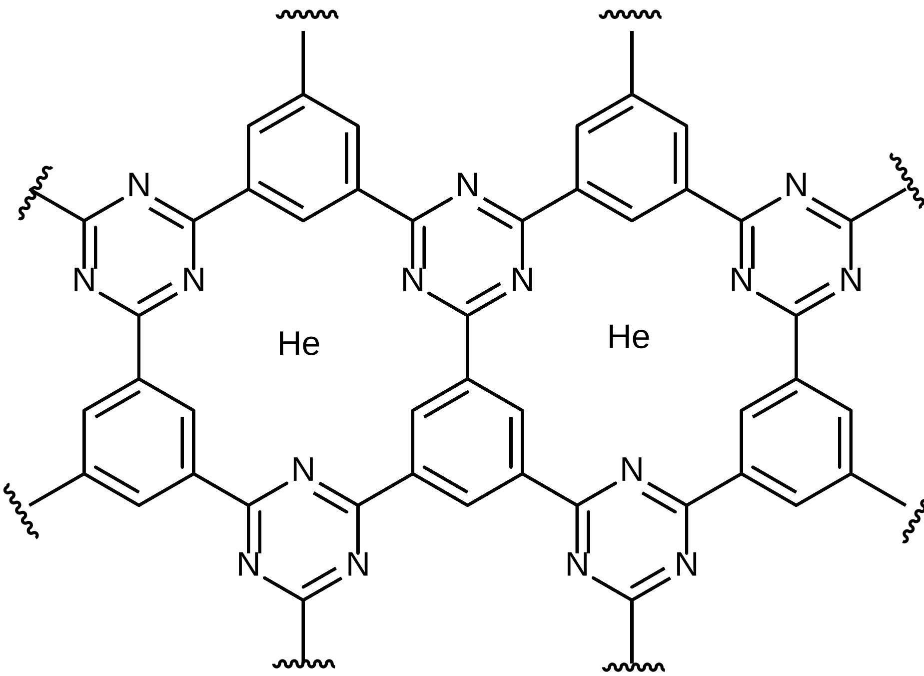
Problem 2 (4 pts).

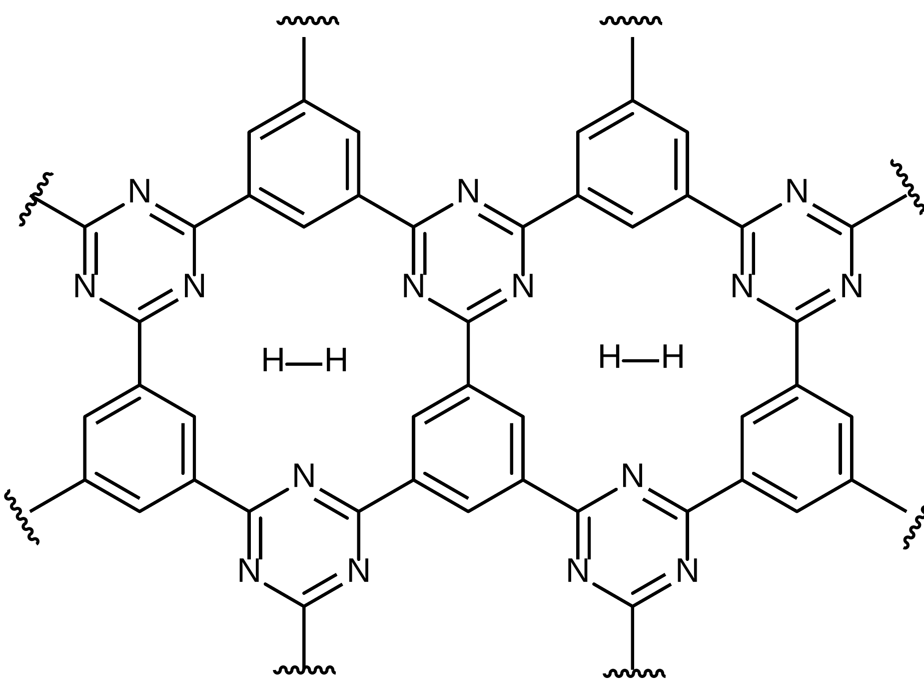
Covalent organic frameworks or COFs are porous materials which extend in two or three dimensions where all building blocks are linked by strong covalent bonds. Common methods for COF synthesis involve dehydration of boronic acids, triazine based cyclotrimerization and condensation of anilines with aldehydes. These materials are being investigated for gas storage and separations as well as their interesting optical and electrical properties. For the 2-D COFs shown below, assign the 2-D symmetry group, label the symmetry elements and mark the smallest possible unit cell and the corresponding asymmetric unit.

A) Pictured below is COF-1 which is synthesized by dehydration of benzene-1,4-diboronic acid. If the lattice is hexagonal or centered rectangular, draw the higher symmetry unit cell(s) in addition to the primitive cell.

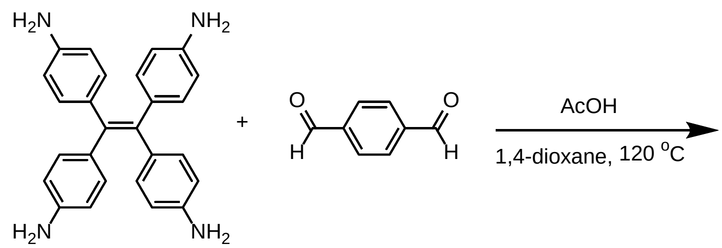

(HO)2B
B(OH)2
-H2O

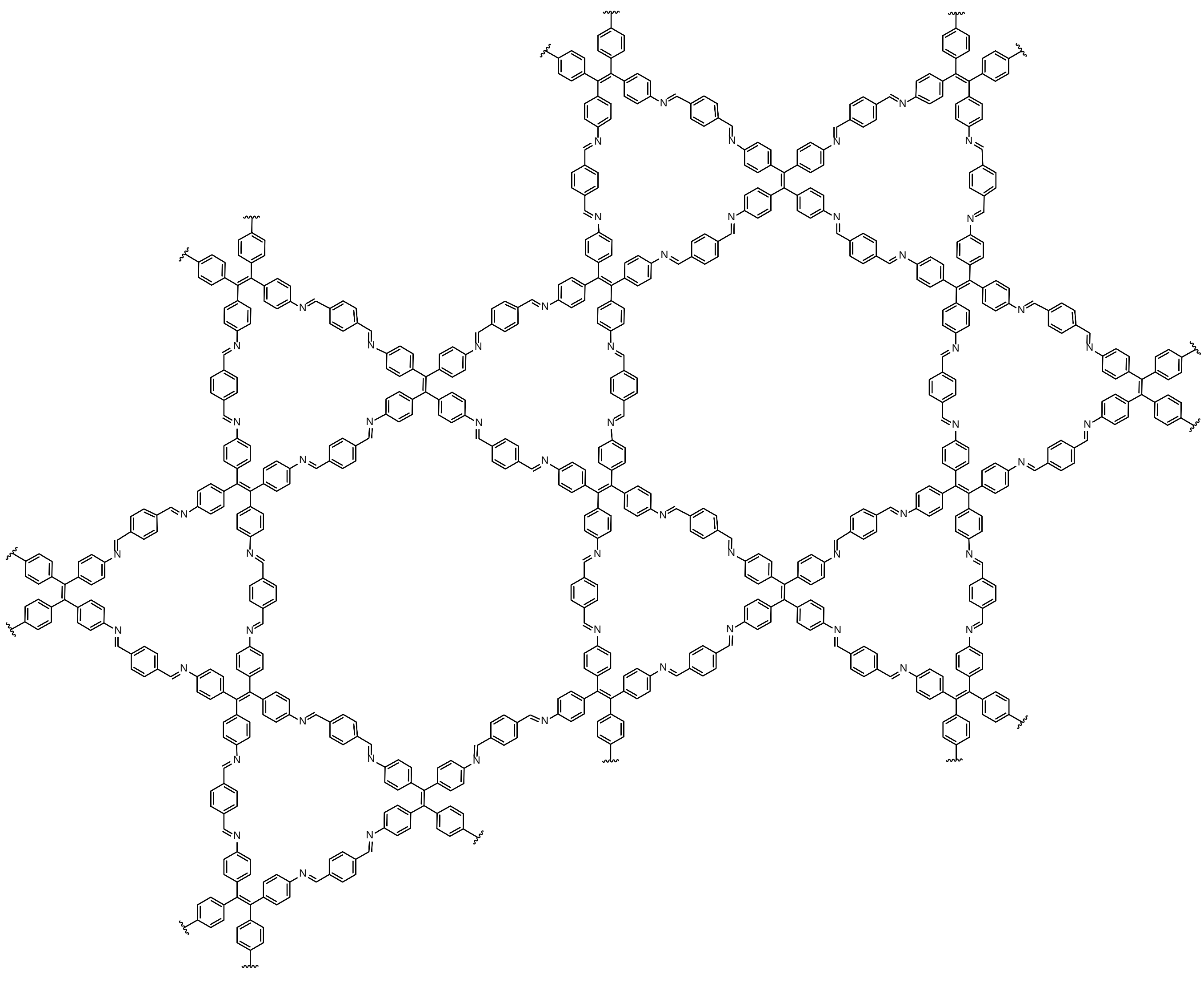
B) A COF synthesized by cyclotrimerization of 1,3,5-tricyanobenzene (CTF-0) is shown below. A recent study on CFT-0 by Zhong *et. al.* (ACS Appl. Mater. Interfaces 2016, 8, 8694) investigated it's utility for separation of He and H_2 gases. Consider the structures shown below where He or H_2 resides within the pores.



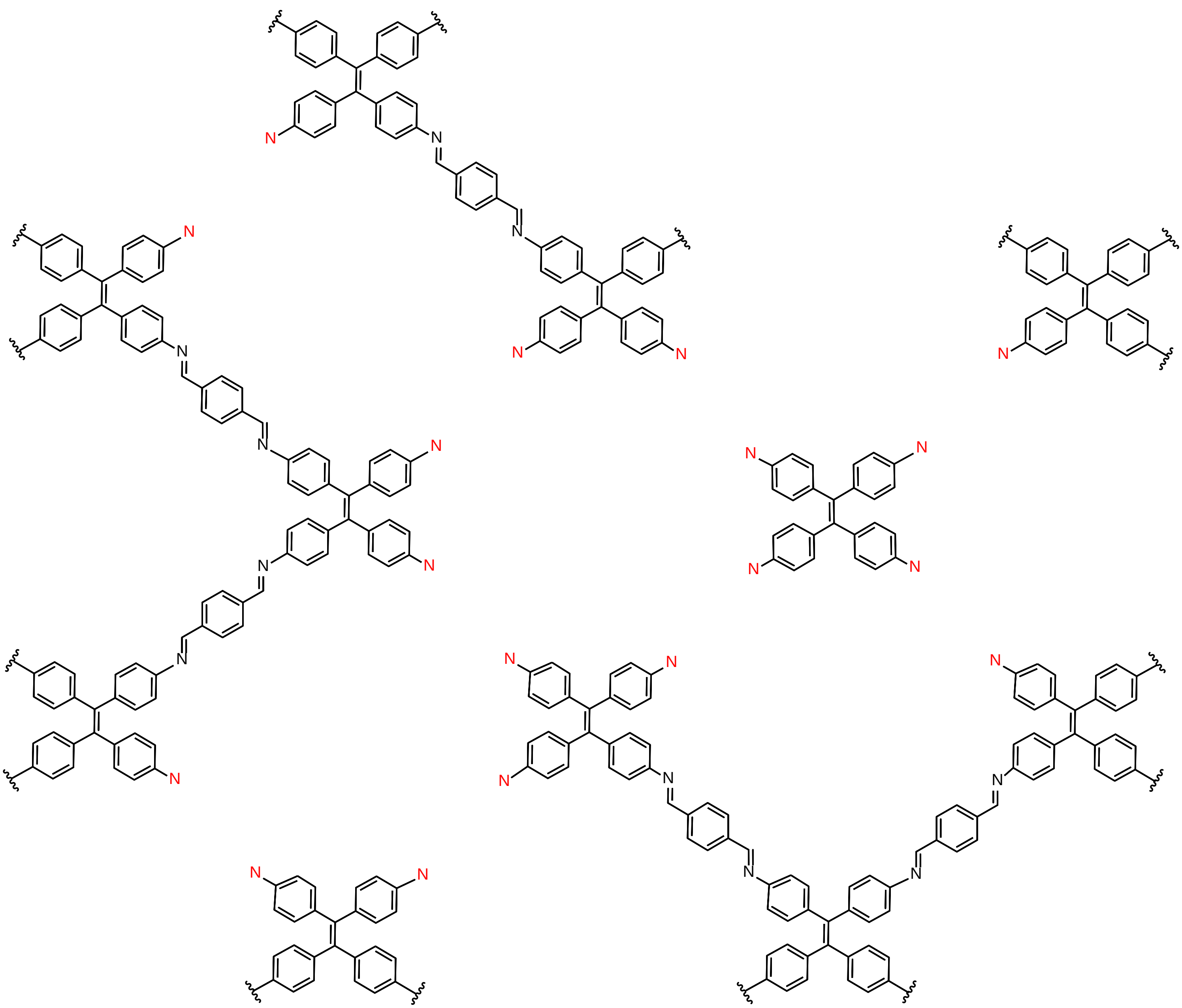


C) A recent paper from Zhao *et. al.* (*J. Am. Chem. Soc.*, 2016, *138* (14), pp 4710) reported synthesis of several COFs via condensation of 4,4',4'',4'''-(ethane-1,1,2,2-tetrayl)tetraaniline (ETTA) with terepthalaldehyde (TPA) and [1,1'-biphenyl]-4,4'-dicarbaldehyde (BPDA). There are two possible structures for the COF formed from ETTA and TPA, one of which has two different pore sizes and one where all pores are the same size. The structure with multiple pore sizes (COF-BPDA) is shown below.

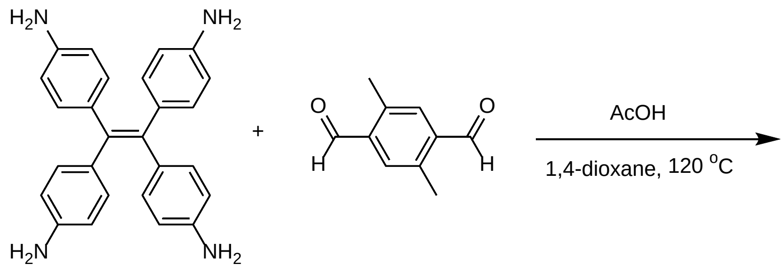


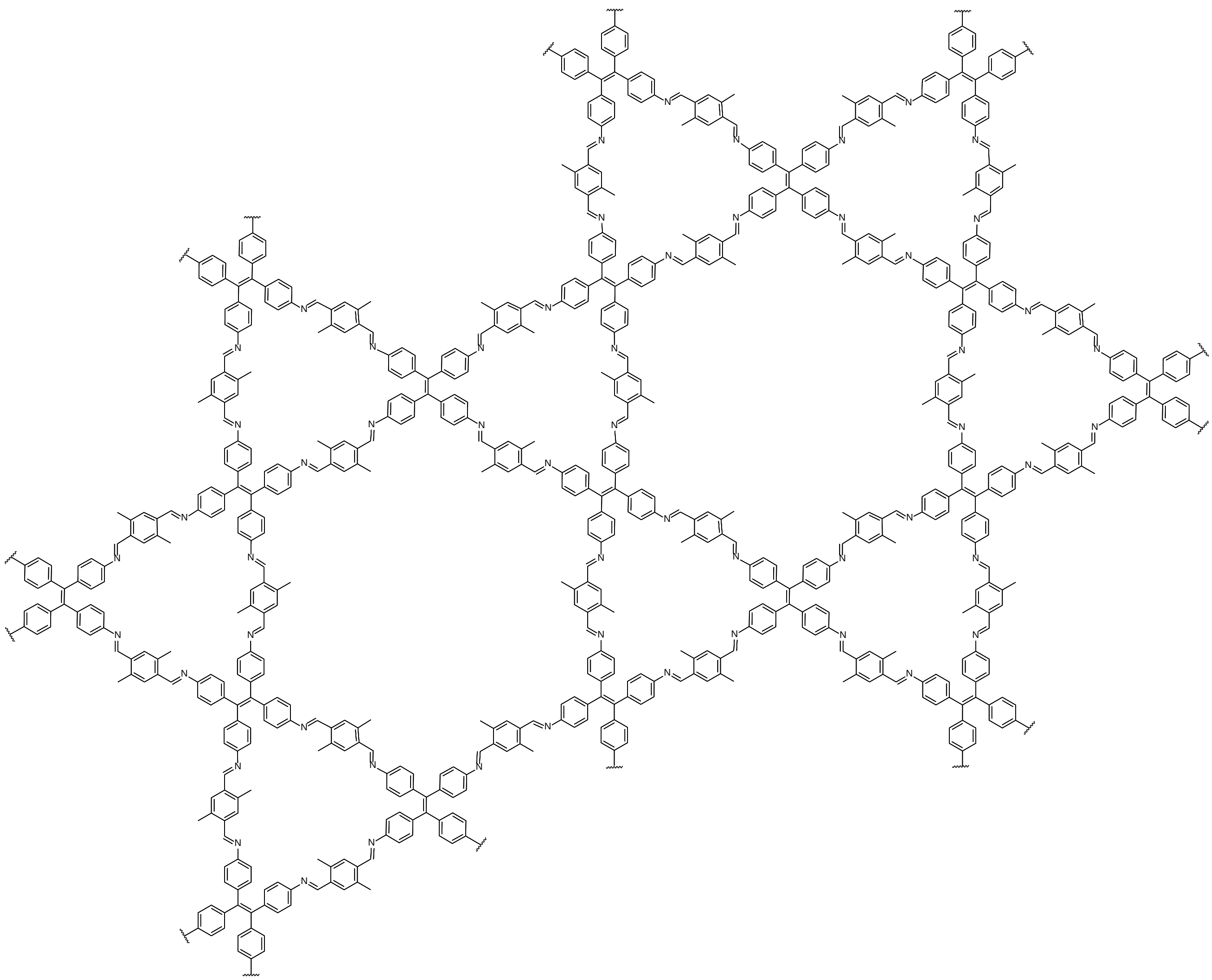


D) Another possible structure from starting materials used in part C has all pore sizes the same and belongs to the plane group cmm. An incomplete representation of this structure (SP-AA) is shown below. Fill in the imine linkers between the shown portions of SP-AA in order to generate a structure belonging to cmm. Show that the structure you have generated for SP-AA belongs to cmm by labelling the symmetry elements, unit cell and asymmetric unit. (Note: The imine nitrogens where a linker must be filled in are highlighted in red).

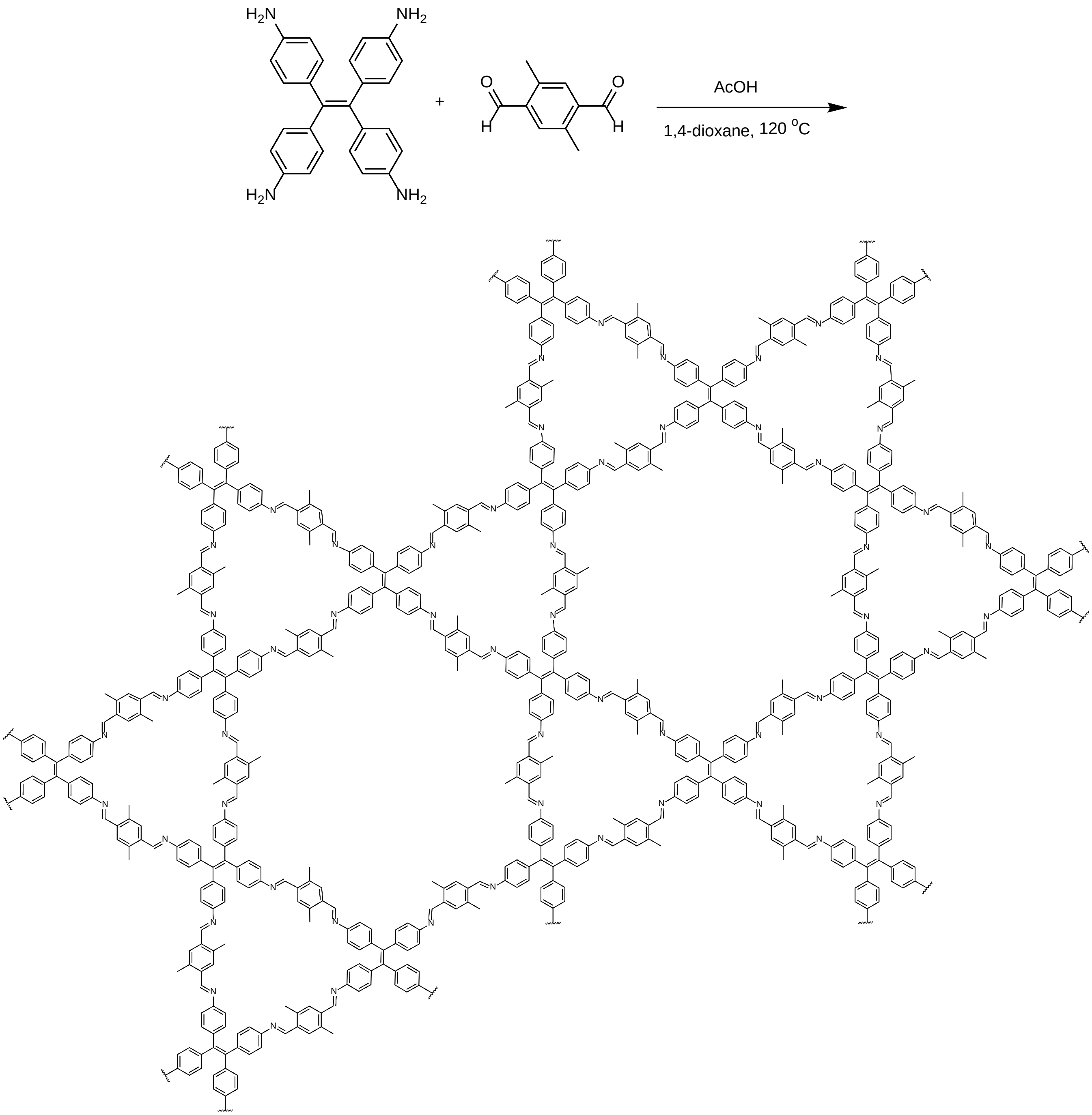


E) A hypothetical derivative of COF-BPDA with a methylated terepthalaldehyde is shown below.



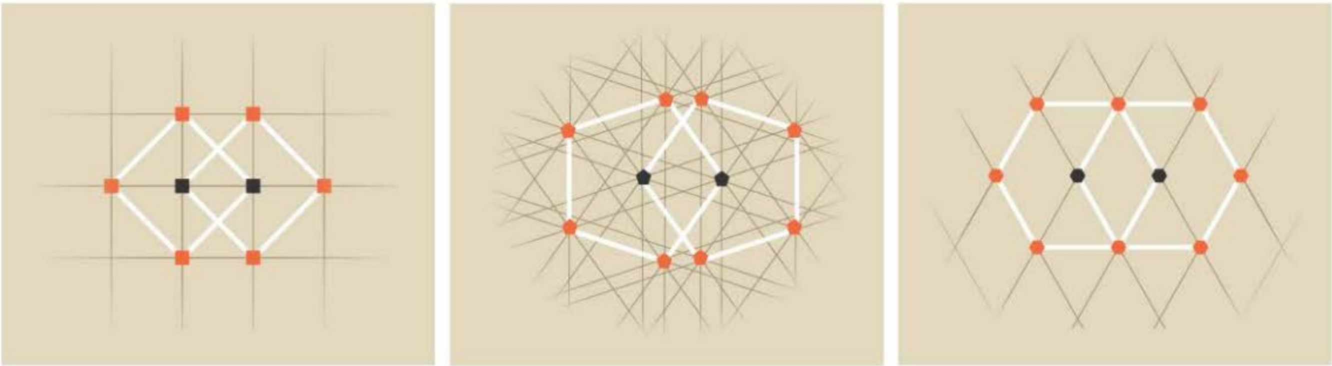


F) A structure related to the COF shown in part E is shown below.



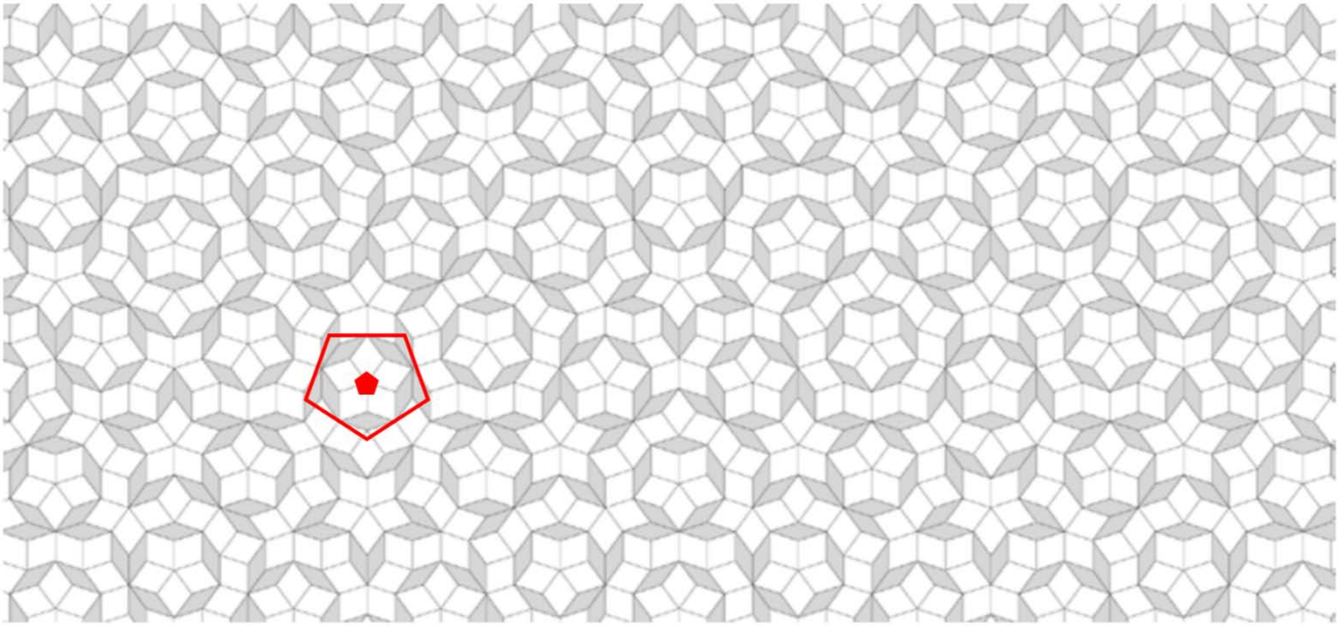
Problem 3. (1 points)

Rotational symmetry in a crystal (3D) or plane (2D) is usually limited to 2-fold, 3-fold, 4-fold, and 6-fold symmetries. As proof, consider how two parallel 4-fold and 6-fold rotation axes generate translational symmetry, while two parallel 5-fold rotation axes clearly cannot generate periodicity, hence crystallinity.

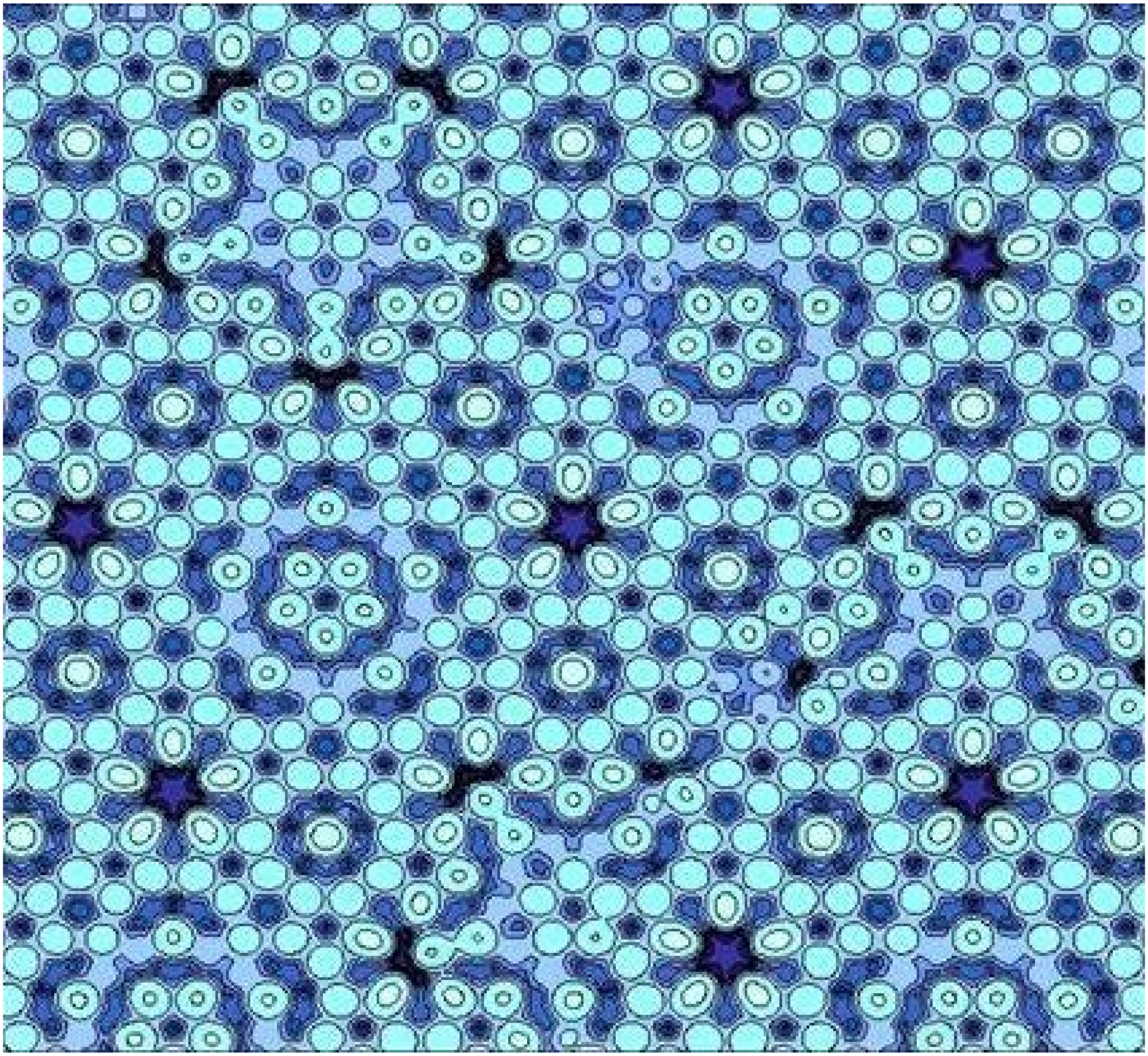


The Nobel Prize in chemistry in 2011 was awarded to Dan Shechtman for the discovery of quasicrystals. Such materials have an ordered structure, generating Bragg diffraction patterns typical of crystals, but lack translational symmetry. Quasicrystals may possess 5-fold, 8-fold, 10-fold, and 12-fold symmetries! The International Union of Crystallography has since changed the definition of a crystal as any solid having a discrete diffraction pattern.

1) For the pattern shown below, locate and assign the order of all *unique* local rotation axes and reflection planes. Draw the largest possible boundary around each local rotation axis to show your answer. An example of a local 5-fold rotation axis is shown below. For this exercise, find local rotation axes with boundaries larger than the one shown below.



2) For the pattern shown below, locate and assign the order of all *unique* local rotation axes and reflection planes. Draw the largest possible boundary around each local rotation axis to show your answer.



Problem 4. (2 points)

Pick a topic of interest from the recommended reading in bold. Prepare two power point slides including relevant descriptive chemistry (background on synthesis, applications, reactivity, properties, trend, etc, as applicable), some concepts presented in class (point group assignment, symmetry elements, etc) and some application of the provided software (for example, highlight symmetry elements / operations). Turn in a printout of the slides with your problem set, and email the TAs the slides in pdf format by 12:00 noon on the due date. Please format file names as “FirstName_LastName_PSET#” and include your name on the first slide.