

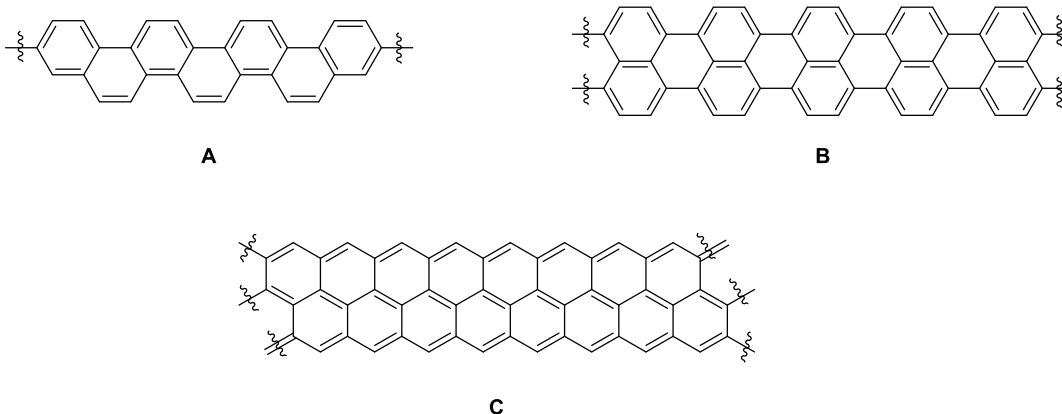
Recommended reading: 16.7-16.10 (3rd/4th edition)

2015/2016 Ch 102 – Problem Set 2

Due: Thursday, April 14 – Before Class

Problem 1. (4 points)

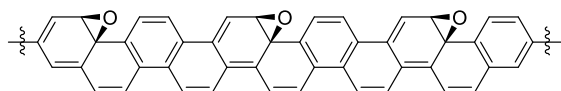
Graphene is a two-dimensional carbon allotrope, consisting entirely of sp^2 hybridized carbons. Although the three-dimensional graphite has been known and used for centuries, it was not until 2004 that two-dimensional graphene was synthesized via mechanical exfoliation of graphite sheets (Nobel Prize Physics, 2010). Graphene exhibits intriguing electronic and thermal properties, owing to its extensive delocalized pi-system. These unique properties have led to increased interest in other low-dimensional all-carbon materials, including one-dimensional strips of graphene sheets known as graphene nanoribbons (GNRs):



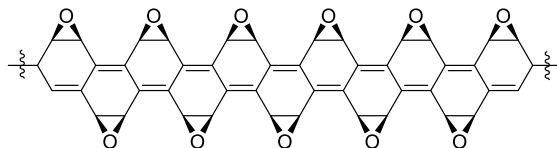
As shown above, GNRs can vary in both shape and size. The shape depends on the edge pattern of the ribbon and can either be armchair as in **A** or **B**, or zigzag as in **C**. Additionally, the width of the ribbon can be varied and GNRs of 4 carbon width (**A**), 5 carbon width (**B**), and six carbon width (**C**) can be envisioned. Theoretical models have predicted highly varied electronic properties for each of these materials, with large band gaps and insulating properties predicted for **A**, small band gaps and semi-conductor type properties for **B**, and unique spin states localized on the zigzag edges of **C**. Liljeroth et al. in 2015 were able to successfully synthesize nanoribbons with structure **B** and experimentally confirmed its near-metallic band gap. (Liljeroth et al. *Nature Comm.* **2015**, 6, 10177.)

- a) Provide the symmetry elements present in **A**, **B**, and **C** and determine their 1-D symmetry classes. Additionally, indicate the unit cell and asymmetric unit for each. Assume a fully delocalized pi-system with all C-C bonds the same length.

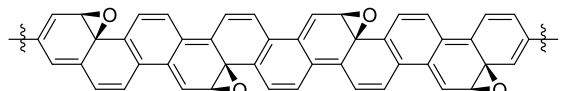
Graphene can be oxidized to give graphene oxide species, effectively epoxidizing double bonds within the sp^2 -hybridized network. Envisioning the analogous oxidation of GNRs **A**, **B**, and **C** gives a variety of possible graphene nanoribbon oxides (GNROs) including:



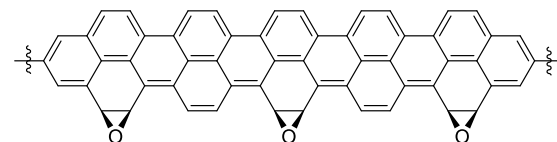
D



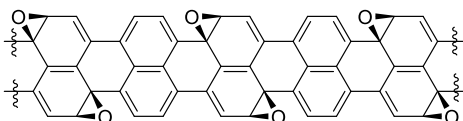
E



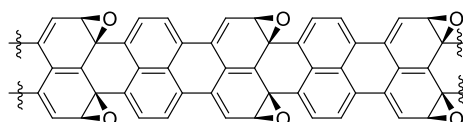
F



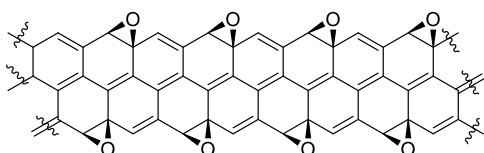
G



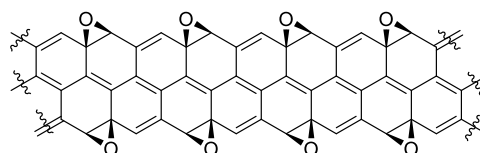
H



I



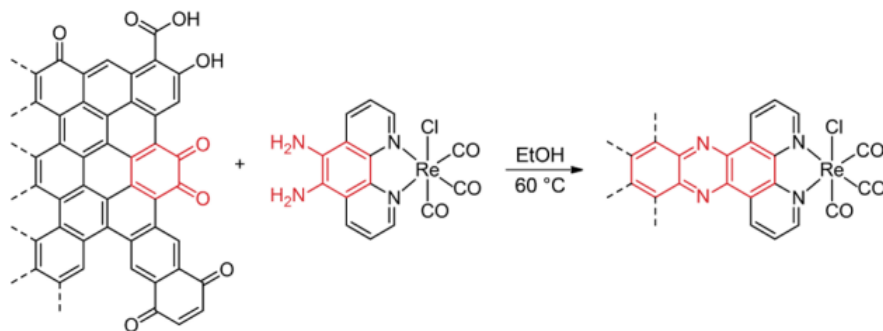
J



K

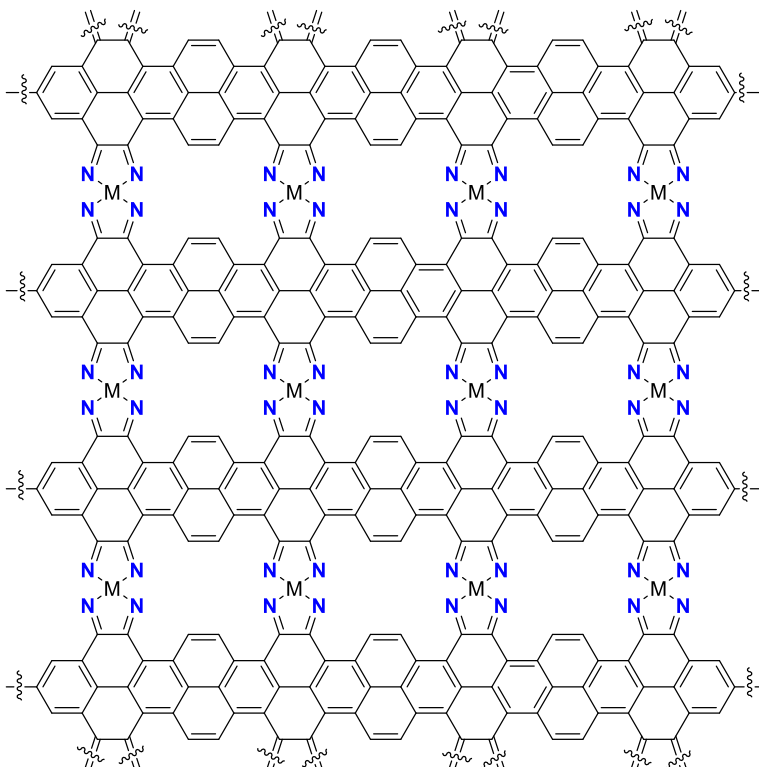
b) For each of GNROs **D**, **E**, **F**, **G**, **H**, **I**, **J**, and **K**, please provide all symmetry elements present and determine their 1-D symmetry class. Additionally, please indicate the unit cell and asymmetric unit for each.

In 2016, Surendranath et al. reported the functionalization of orthoquinone sites along arm-chair edges of graphene sheets in glassy carbon electrodes in order to attach rhenium catalysts for the reduction of CO₂ to CO. (Surendranath et al. *J. Am. Chem. Soc.* **2016**, 138, 1820.)

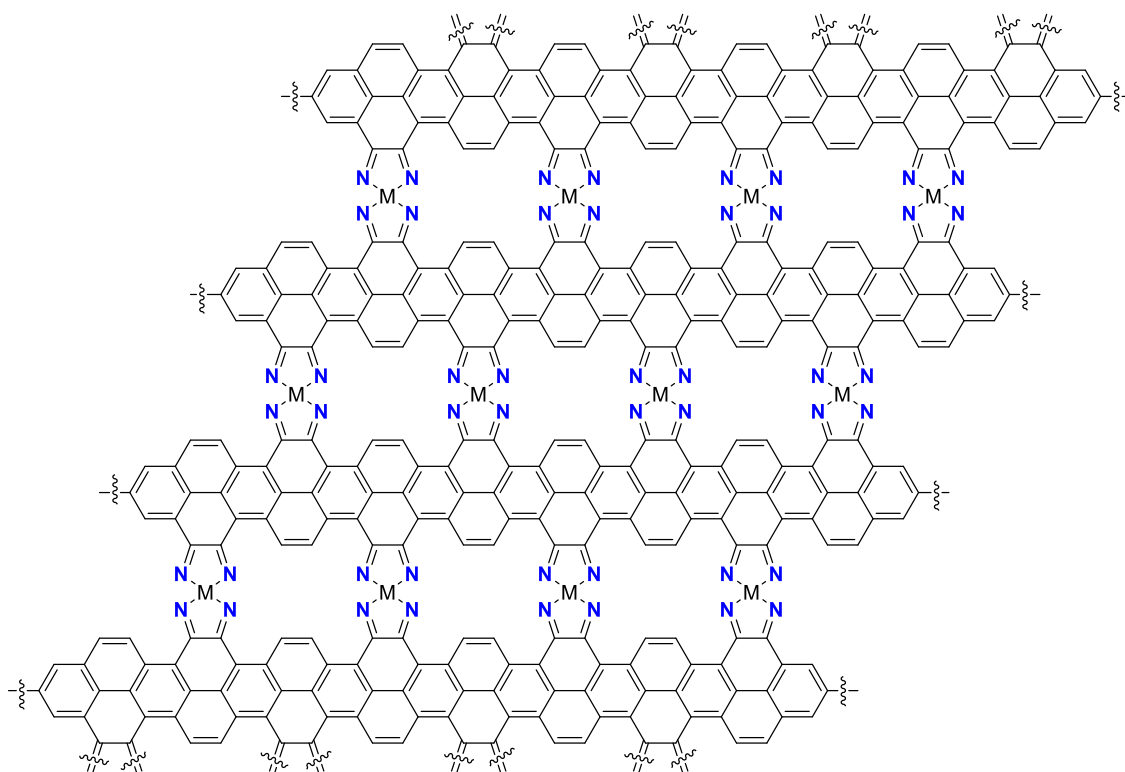


One can similarly envision functionalizing the edges of armchair GNRs **A** and **B** with ortho-iminoquinones and mixed N/O donor quinone structures. These sites could then bind metal centers (M), generating two-dimensional networks of metal-tethered GNRs as shown in the examples below:

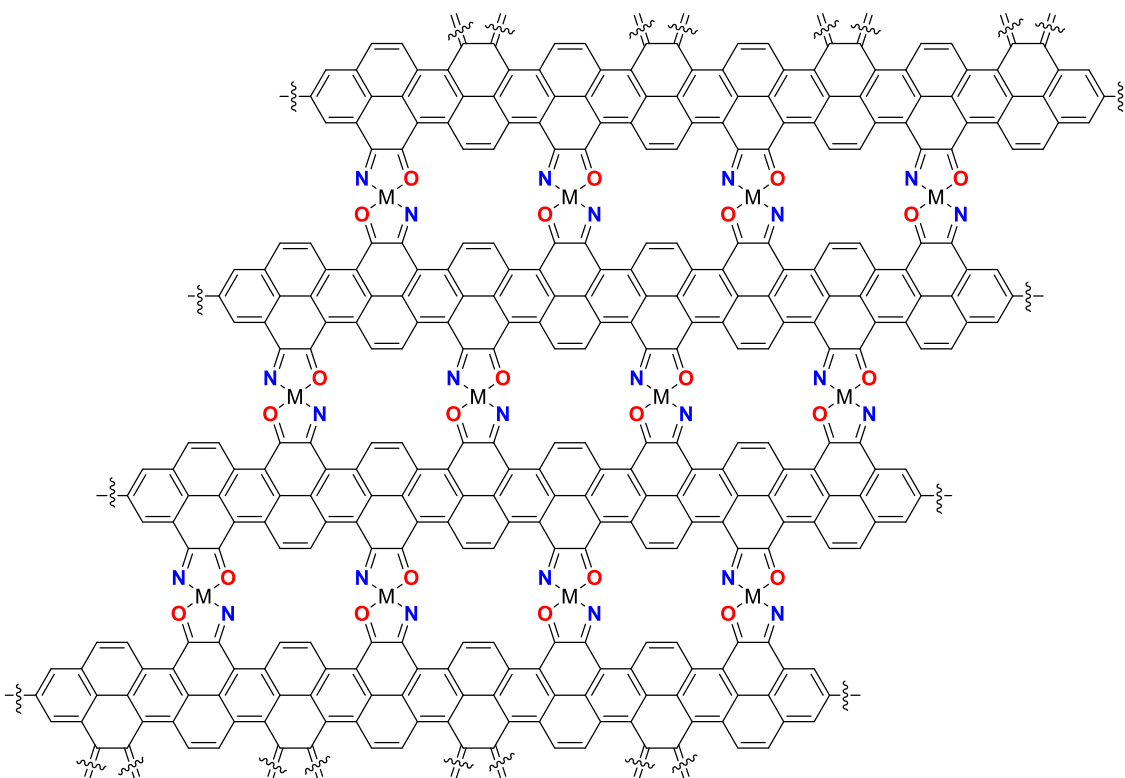
c) For each two-dimensional structure **L-P**, please denote the symmetry elements present, the 2-D symmetry class, and indicate the unit cell and asymmetric unit.



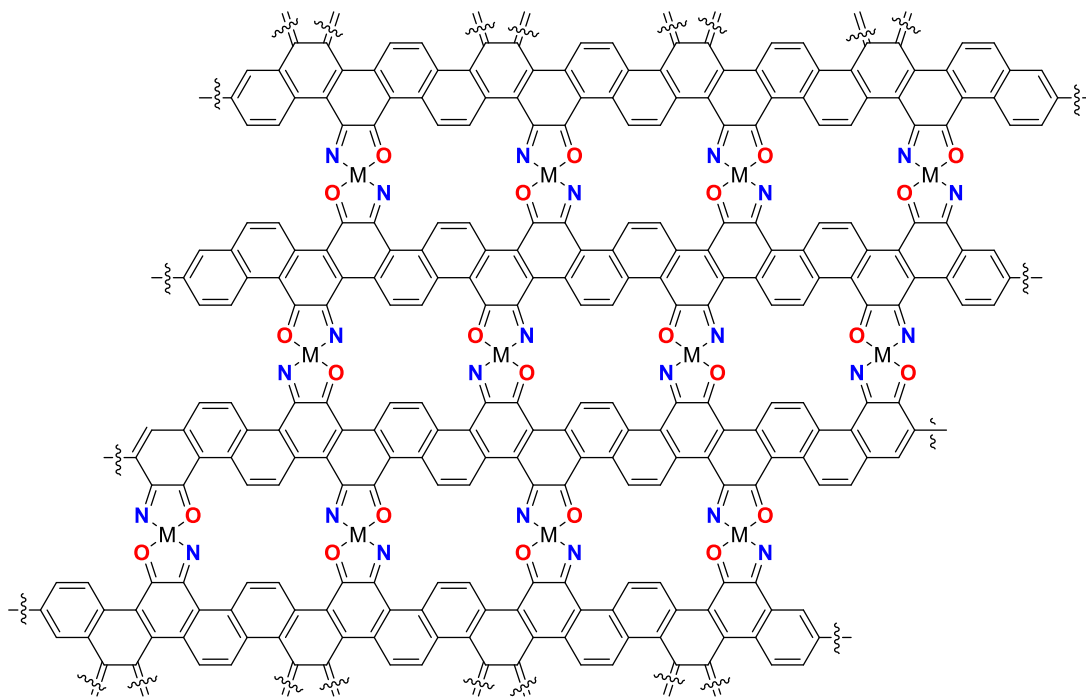
L



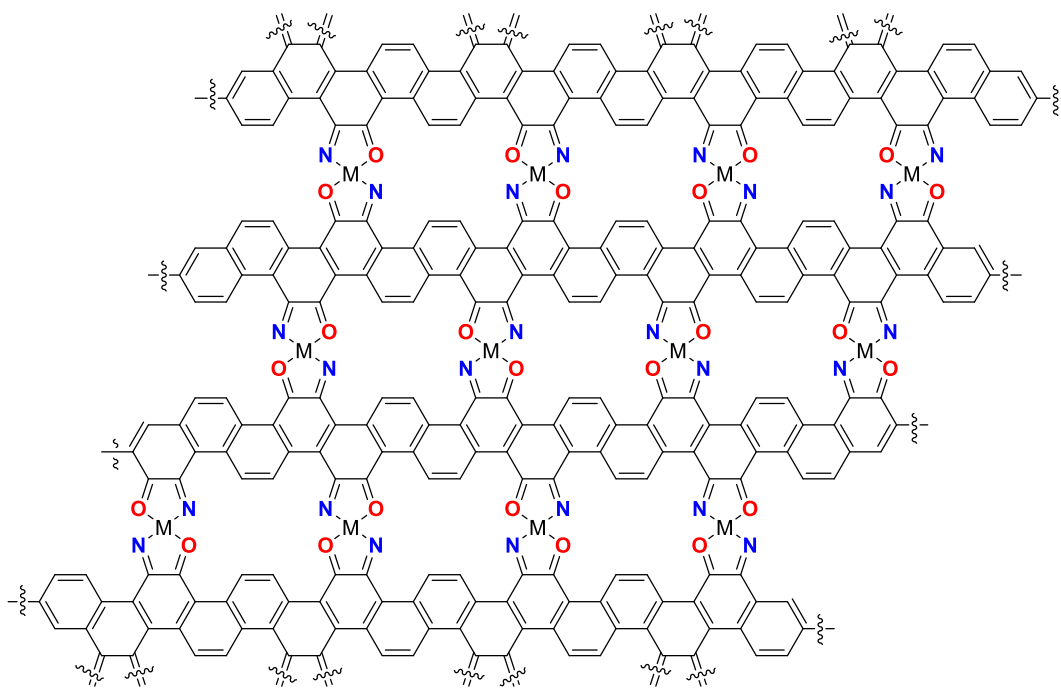
M



N



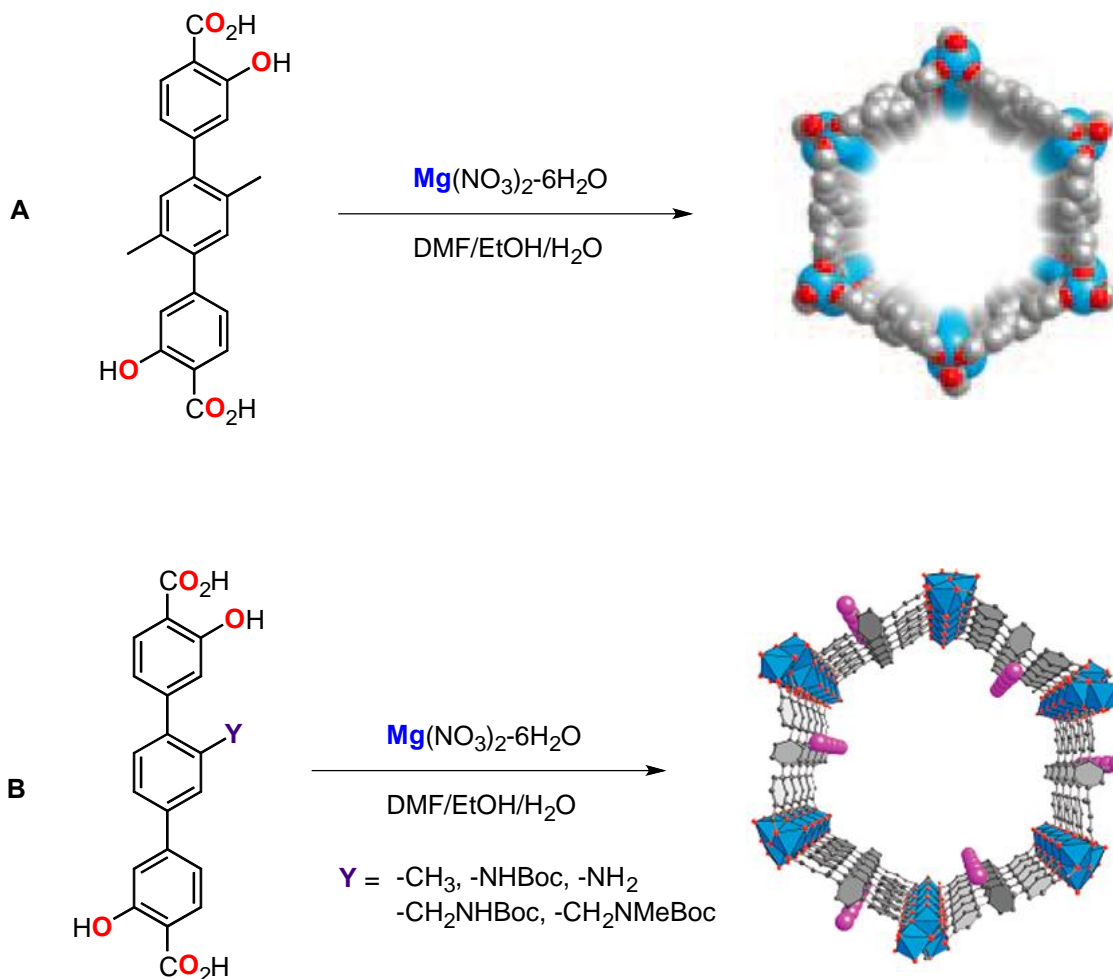
O



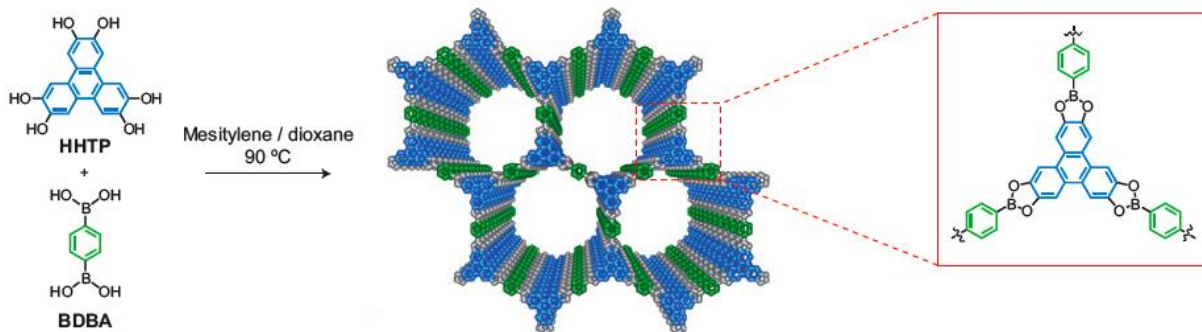
P

Problem 2. (1 point)

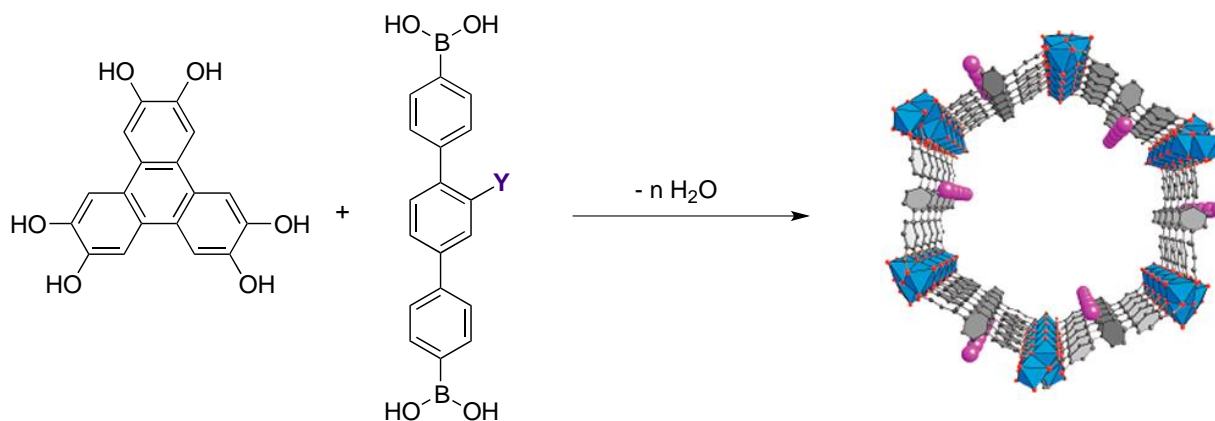
Metal-Organic Frameworks (MOFs) have potential applications in gas storage and release, gas separations and purifications, and catalysis. The ter-phenyl linker **A** below has been shown to react with Mg^{2+} to yield a hexagonal 2-D MOF, and substitution in **B** results in MOFs that reversibly store CO_2 .



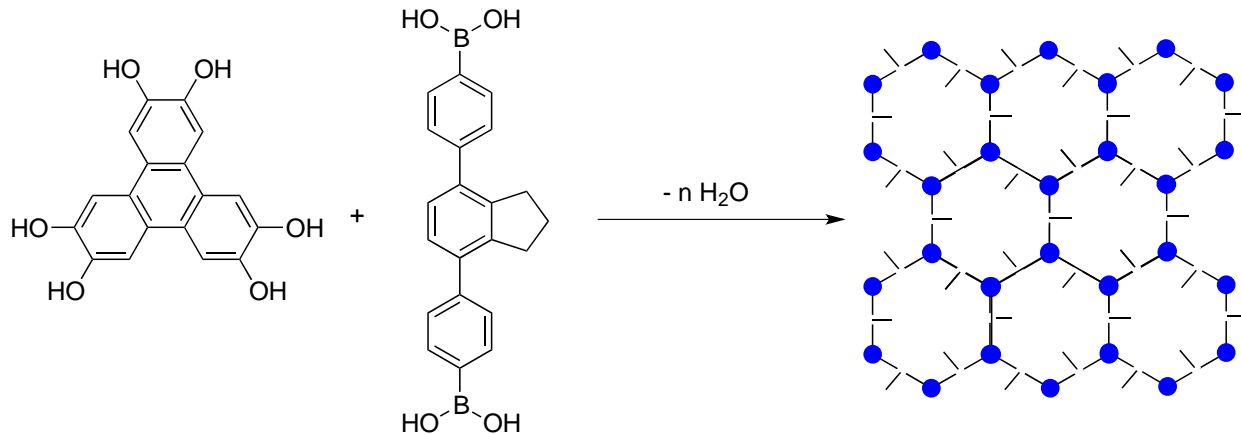
Similar two and three-dimensional structures can also be generated in the absence of metal ions through covalent interactions. These materials are referred to as Covalent Organic Frameworks, or COFs. COFs can have properties similar to MOFs as they can both develop pores of different sizes. Additionally, through choice of organic fragments, COFs can demonstrate unique electronic properties.



- a) Determine the 2-D space group of the lattice derived from benzene-1,4-diboronic acid (**BDBA**) and 2,3,6,7,10,11-hexahydroxyterphenylene (**HHTP**), and show the unit cell and asymmetric unit.



- b) Similarly, determine the 2-D space group of the lattice derived from the asymmetric linker shown above ($Y \neq H$). Assume that Y alternates in a manner similar to what is observed from the MOF of **G**. Determine the 2-D space group, show the symmetry operations, unit cell, and asymmetric unit. What symmetry elements are lost going from $Y = H$ to $Y \neq H$?

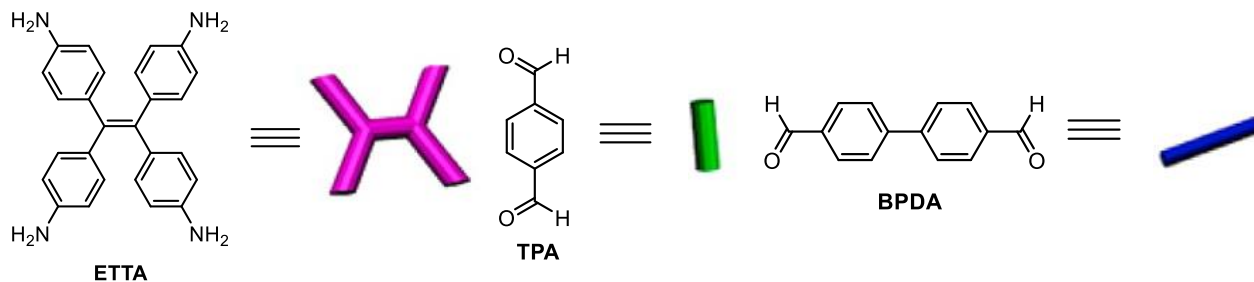


- c) Determine the 2-D symmetry of the lattice derived from the asymmetric linker shown above. Assume the central aromatic ring alternates in a manner similar to part b. Show the symmetry operations, unit cell, and asymmetric unit. What symmetry elements are present here that are not present in part b?

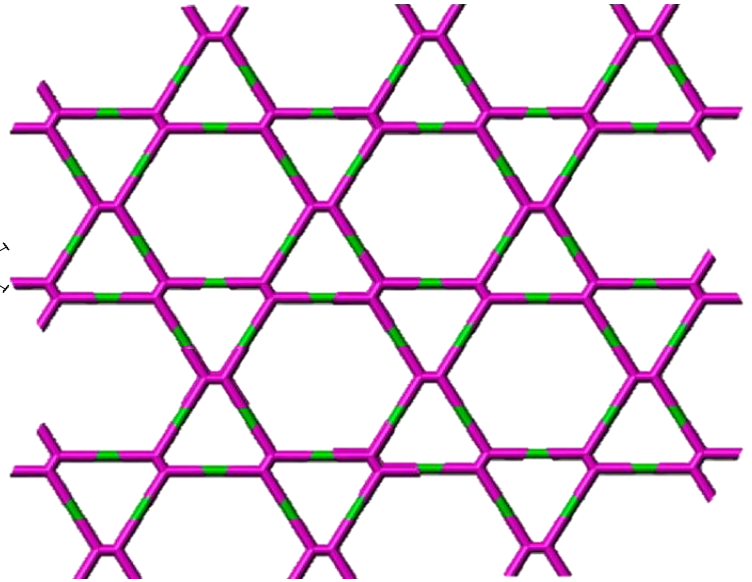
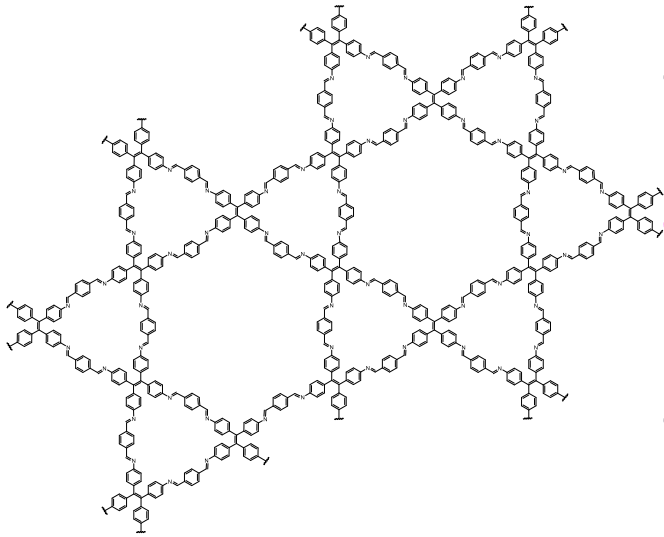
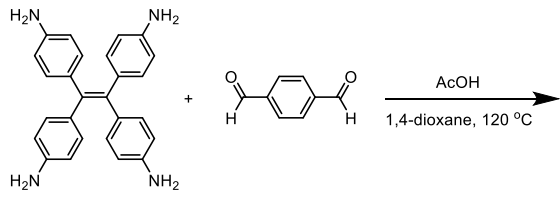
Problem 3. (3 points)

Recently, Zhao and co-workers have reported the synthesis of Covalent Organic Frameworks (COFs) that can contain up to three different pore sizes (*J. Am. Chem. Soc. Article As Soon As Publishable*, DOI: 10.1021/jacs.6b01244). One example, called **COF-BPDA** (see below), is made through the reaction of 4,4',4'',4'''-(ethane-1,1,2,2-tetrayl)tetraaniline (**ETTA**) and terephthalaldehyde (**TPA**) in 1,4-dioxane with acetic acid. The resulting yellow powder was characterized with powder X-ray diffraction to have a structure consistent with **COF-BPDA**. This data ruled out another possible structure, which contains only one pore size (**SP-AA**, part b). A similar structure containing three different pore sizes (**SIOC-COF-1**, part c) was constructed by reacting **ETTA** with **TPA** and [1,1'-biphenyl]-4,4'-dicarbaldehyde (**BPDA**) in toluene with acetic acid. Considering other potential linkers, new types of structures could be generated, in principle (parts d-f).

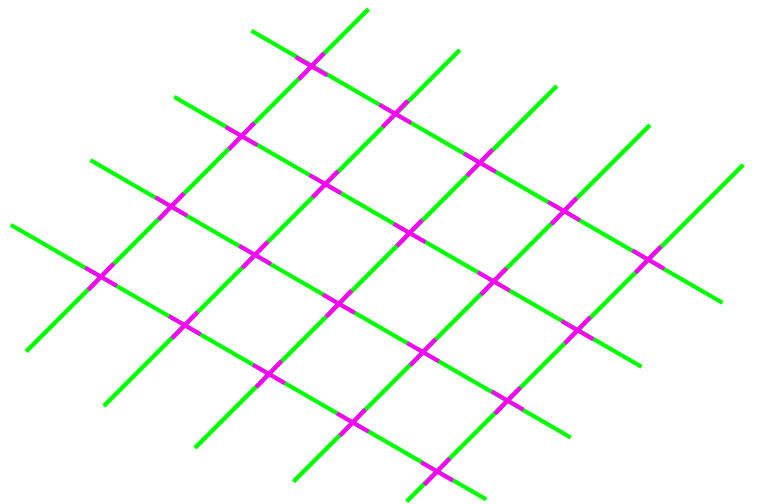
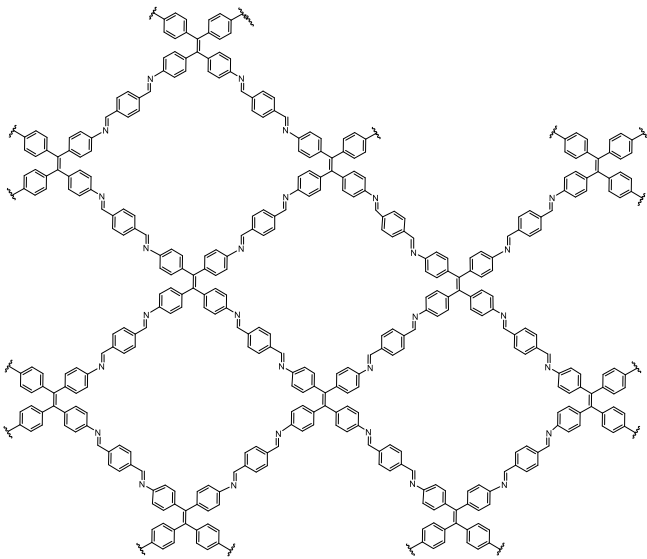
For the following 2D COF's, determine the 2D space group, labelling symmetry elements. Also, mark the (smallest possible) unit cell and asymmetric unit.



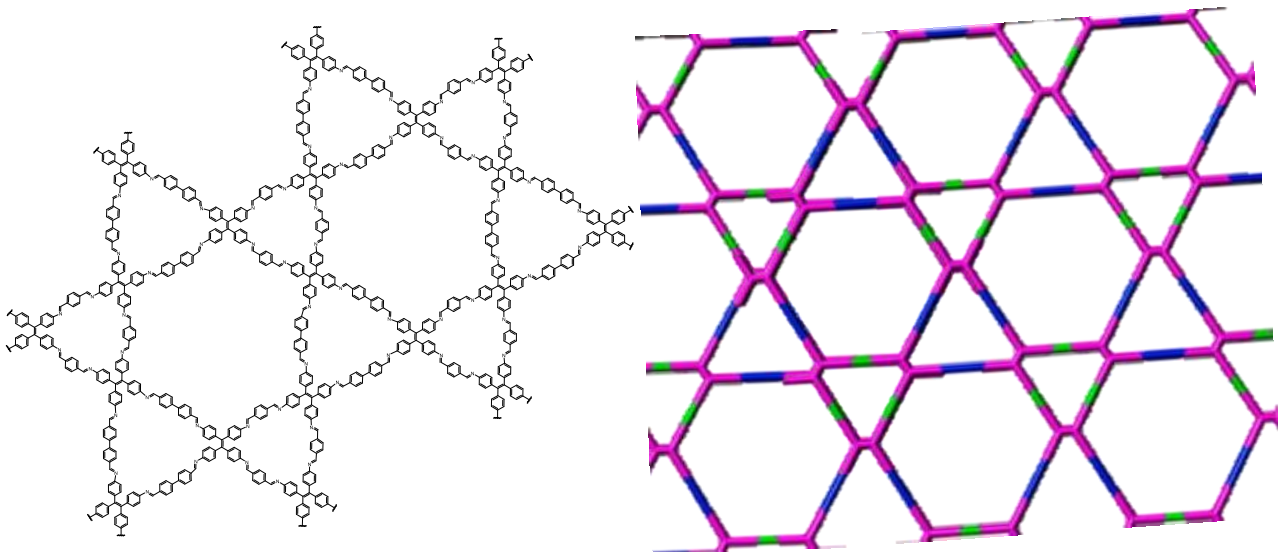
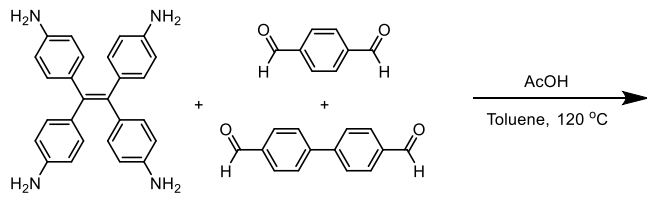
a) COF-BPDA



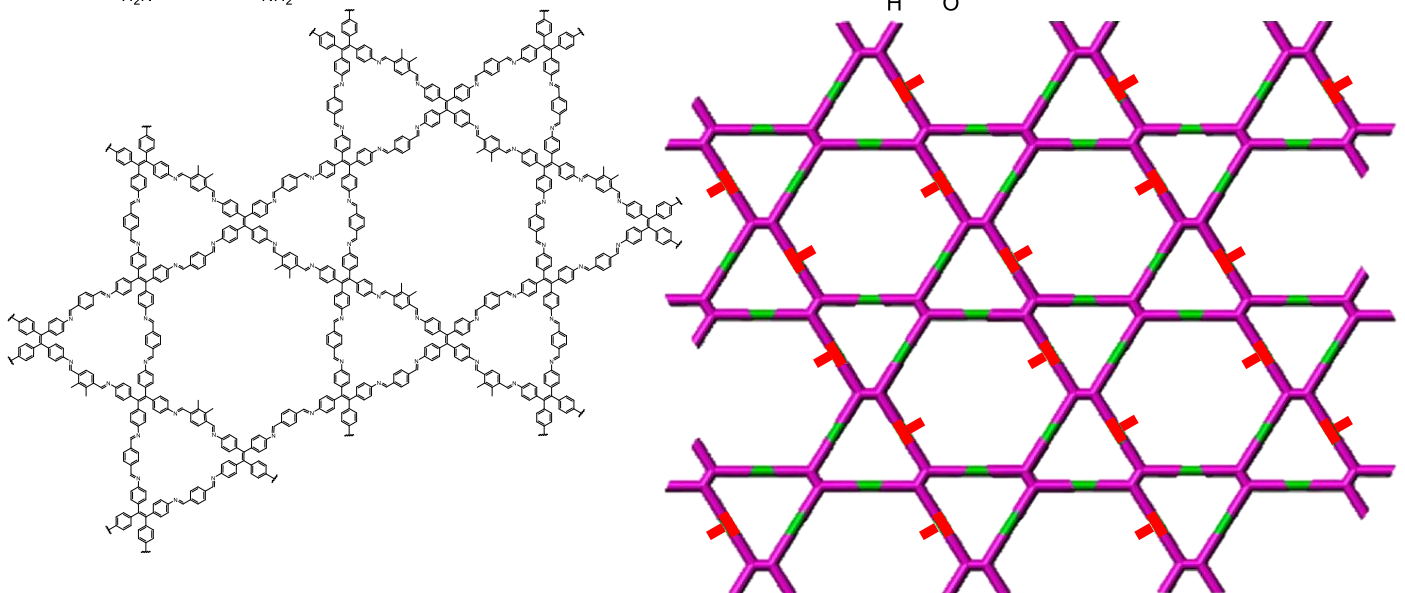
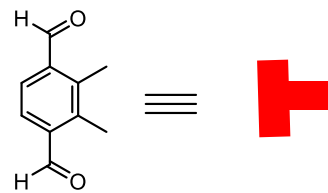
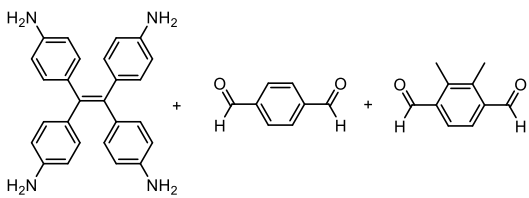
b) SP-AA



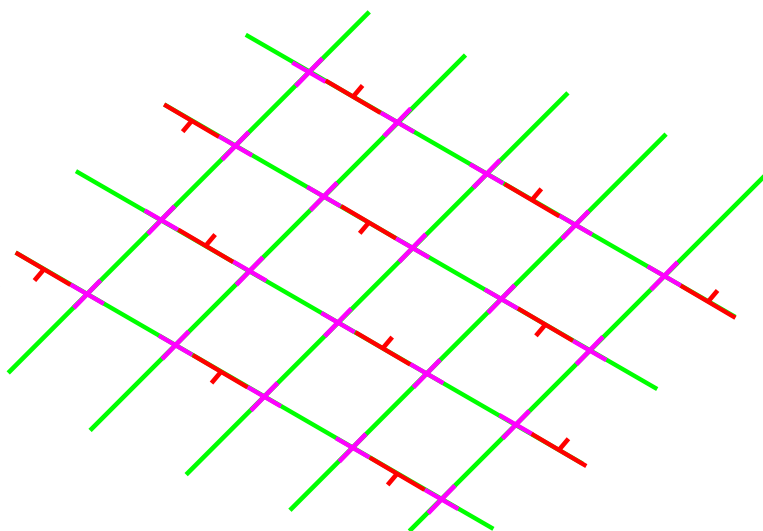
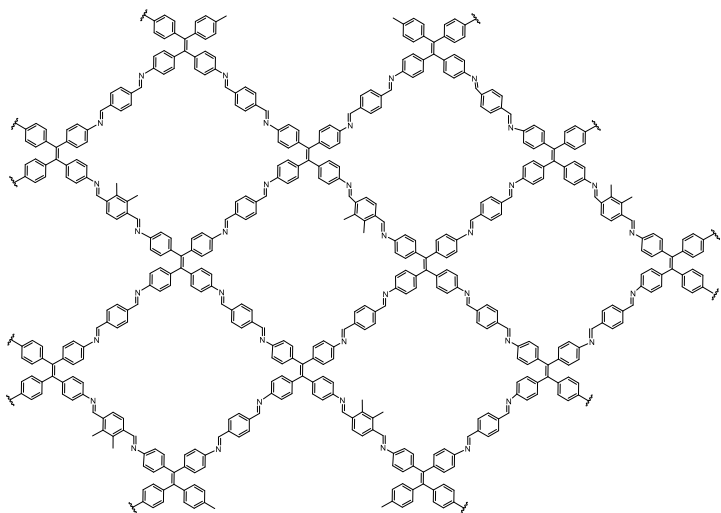
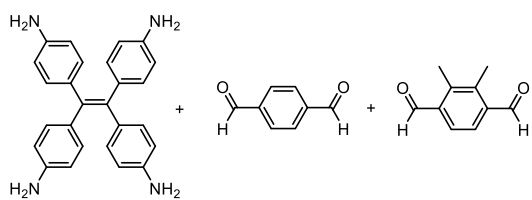
c) **SIOC-COF-1**



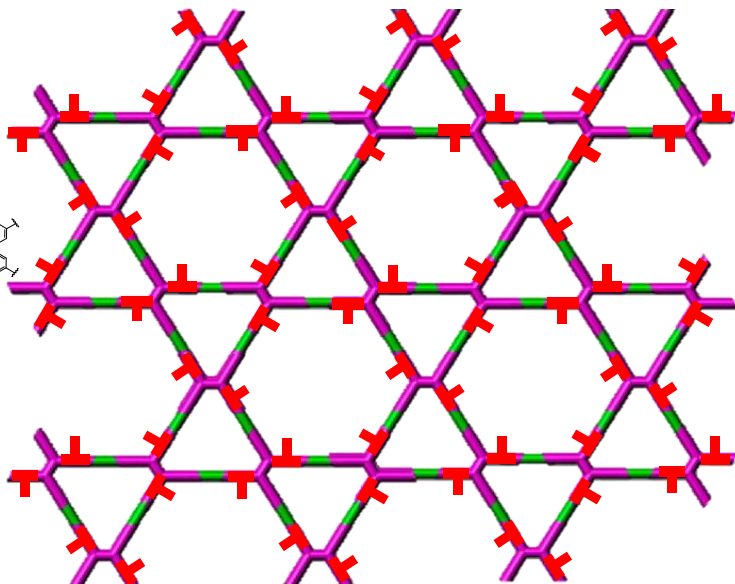
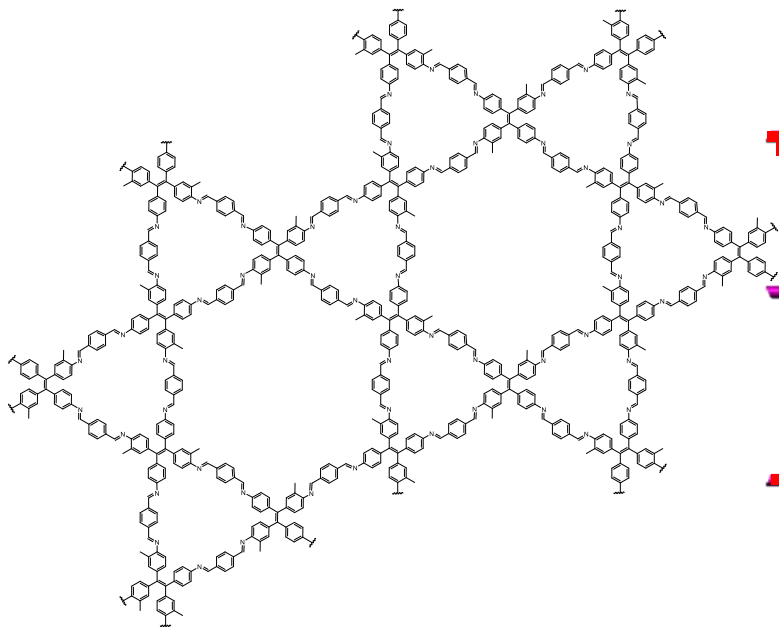
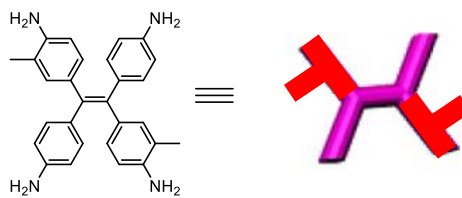
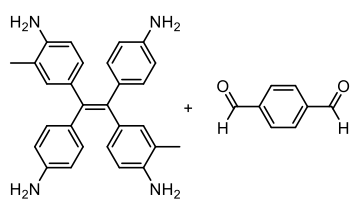
d) **Hypothetical A**



e) Hypothetical B



f) Hypothetical C



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.