Porphyrin-Based Metal-Organic Frameworks

For this activity, we will discuss the literature article "Iron and Porphyrin Metal-Organic Frameworks: Insight into Structural Diversity, Stability, and Porosity," which explores the synthesis, physical structures, and chemical structures of several metal-organic frameworks based around porphyrin ligands. Read through the journal article (Fateeva et al. *Cryst. Growth Des.* **2015**, *15*, 1819-1826), then answer the questions with your group. The relevant crystallographic information files (cifs) can be found in the Supporting Information of the journal article, or on the Cambridge Crystallographic Data Centre (CCDC) Access Structures site (https://www.ccdc.cam.ac.uk/structures/) using the refcodes or DOI from the article.

1) For compounds **2**, $\mathbf{4_A}$, and $\mathbf{4_B}$, fill in the table below with *all* the components that make up 1) the inorganic vertices and 2) the organic linkers and pillars (distinguish these if they are different).

Compound	Inorganic Vertices	Organic Linkers and Pillars
2		
$\mathbf{4_A}$		
$\mathbf{4_B}$		

2) What is meant by pillared paddlewheel structure? State which compound(s) here fit that description.

3) Based on the description and formula of complex **2** in Fig. 2, what do the purple square pyramids represent? The red octahedra?

4) Sketch a "top" view line drawing (with porphyrin ligand in the plane of paper) of one repeating unit, [FeTCPP]$(Fe_2)_4$, of complex **2**. You may omit the bipyridine ligands from the sketch.

5) What does the Mössbauer data for complex $\mathbf{4_B}$ tell you about the structure and composition of the MOF? Describe the coordination number, geometry, and spin state of each iron environment.

6) How do the coordination number, geometry, and spin state of each iron environment in complex $\mathbf{4_A}$ to compare with that of complex $\mathbf{4_B}$? State how many distinct doublets you would expect for the Mössbauer spectrum of $\mathbf{4_A}$, and describe the relative isomer shifts and quadruple splittings you would expect for the doublets (you don't need to give specific values).