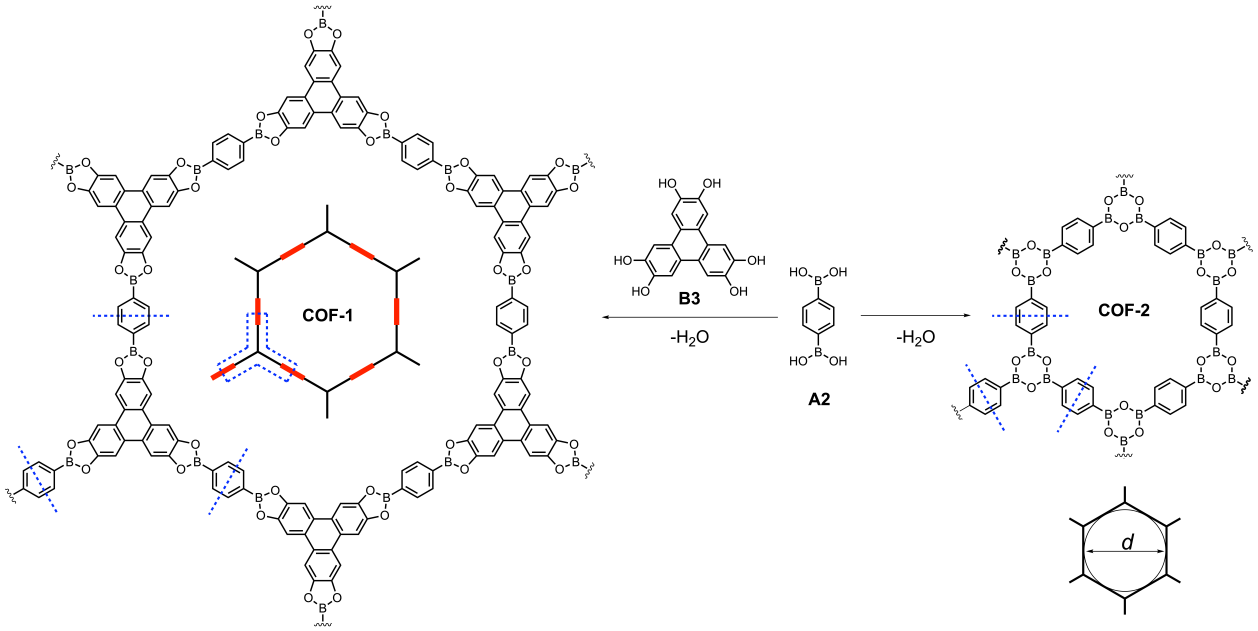
T3. Into Reticular Chemistry

7%							
3.1	3.2	3.3	3.4	3.5	3.6	3.7	∑
2	3	23	12	6	12	5	63

Covalent organic frameworks (COFs) are a class of polymers that form two- or three-dimensional structures through reactions between organic precursors, resulting in covalent bonds to afford porous, crystalline materials. Two examples of honeycomb type 2D-COFs formed by boronate ester and boroxine rings (repeat units indicated using dashed lines) are shown in the figure below.

The black and red bold lines represent different building blocks in all COF topology figures.

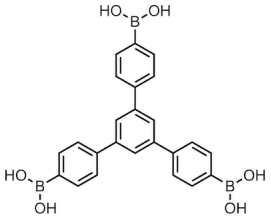


3.1 **Determine** the empirical formula of **COF-1** and **calculate** the mass percentage (%, to two decimal places) of carbon in **COF-1**. 2.0 pt

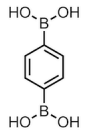
3.2 **Calculate** the internal diameter, *d*, in Å, of the honeycomb for **COF-2**, with the following assumptions: 3.0 pt

- C–C/C=C (arenes) = 1.39 Å
- C–B = 1.56 Å
- B–O = 1.38 Å
- Note, the diameter of a circle, d, inscribed inside a hexagon, is given by $d = \sqrt{3}a$, where a is the side length of the hexagon.
- Neglect the width of the linkers.

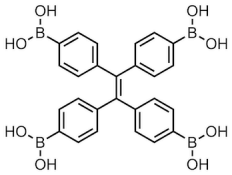
The structures shown below can form 2D and 3D COFs. For this question consider only formation of COFs with boronate esters, imines, and C=C bonds through condensation reactions. **A–E** represent compound classes with different functional groups.



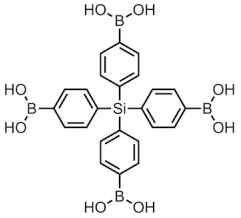
A1



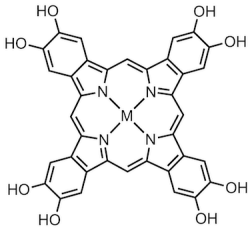
A2



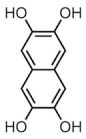
A3



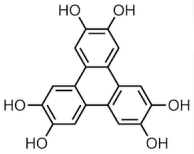
A4



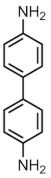
B1



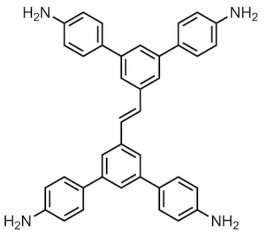
B2



B3



C1



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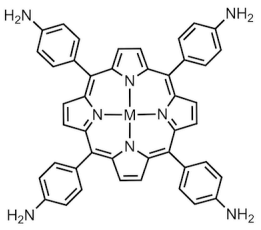
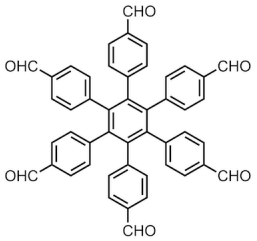
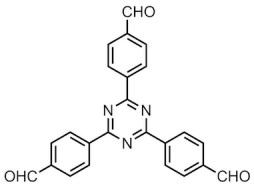


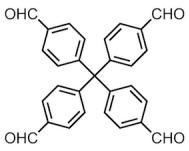
C3



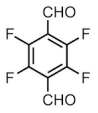
D1



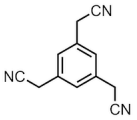
D2



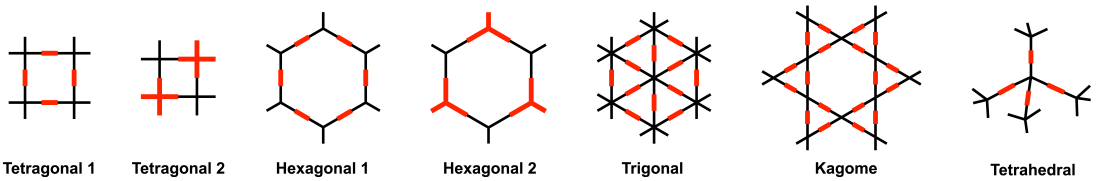
D3



D4



E1



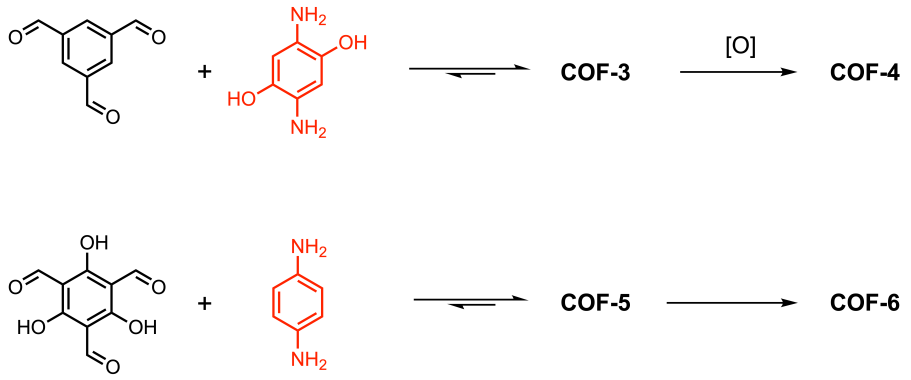
Tetragonal 1 | Tetragonal 2 | Hexagonal 1 | Hexagonal 2 | Trigonal | Kagome | Tetrahedral

Tetragonal means *Tetragonal*, **Hexagonal** means *Hexagonal*, **Trigonal** means *Trigonal*, **Kagome** means *Kagome*, **Tetrahedral** means *Tetrahedral*.

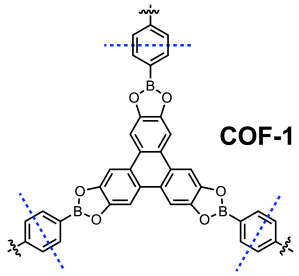
3.3 **Fill all the table** cells with either new examples of monomer combinations that give the topologies shown above or with "**XXX**" if you are certain that no additional combinations satisfy that topology. Both the combinations and the "**XXX**" entries will be graded. Incorrect answers (both combinations and "**XXX**" entries) will be penalised. Blank table cells will not be graded. 23.0 pt

Tetragonal 1	Tetragonal 2	Hexagonal 1	Hexagonal 2	Trigonal	Kagome	Tetra-hedral
		A2 + B3	**E1 + D2**		**C2 + D4**	

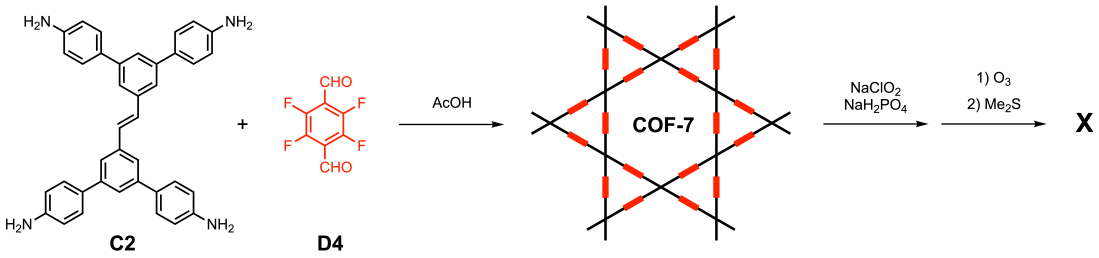
Whilst imine-based COFs are easily synthesised, they are also vulnerable to hydrolysis under strongly acidic and basic conditions. The addition of hydroxy groups to the aldehyde or amine monomers can overcome this. IR spectrum of **COF-3** contained stretches corresponding to the imine functional group, but **COF-4** did not. **COF-4** contains a different type of C=N bonds, and elemental analysis revealed a loss of six additional hydrogen atoms per repeat unit relative to **COF-3** as the only change. **COF-5** irreversibly isomerises to **COF-6**, which did not contain imine stretches in its IR spectrum.



3.4 **Draw** the repeat units for **COFs 3–6.** **Indicate** the edges of each repeat unit with a dashed line as shown for **COF-1** below. 12.0 pt

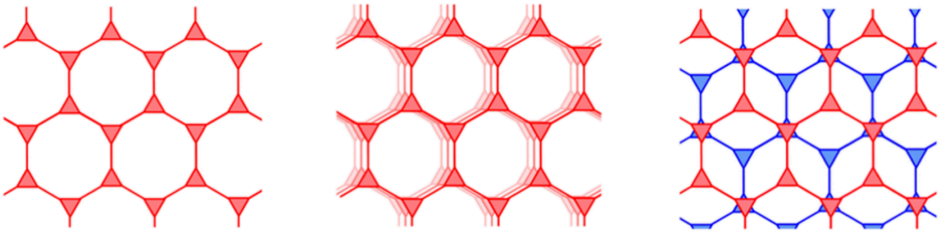


Macrocycle **X** was synthesised by post-synthetic modification of **COF-7** (**C2** + **D4**) followed by degradation.



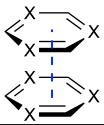
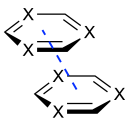
3.5	**Draw** the smallest repeat unit of macrocycle **X**.	6.0 pt

π-π interactions result in different stacking modes of COF layers, some of which are shown below.

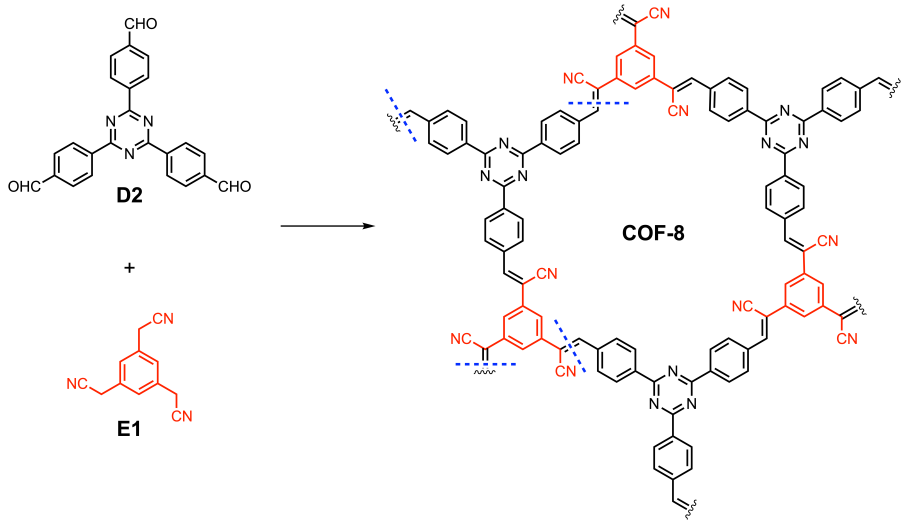


(a) AA (b) AA’ (c) AB

Depending on stacking geometry, the interaction energy can be different as shown below.

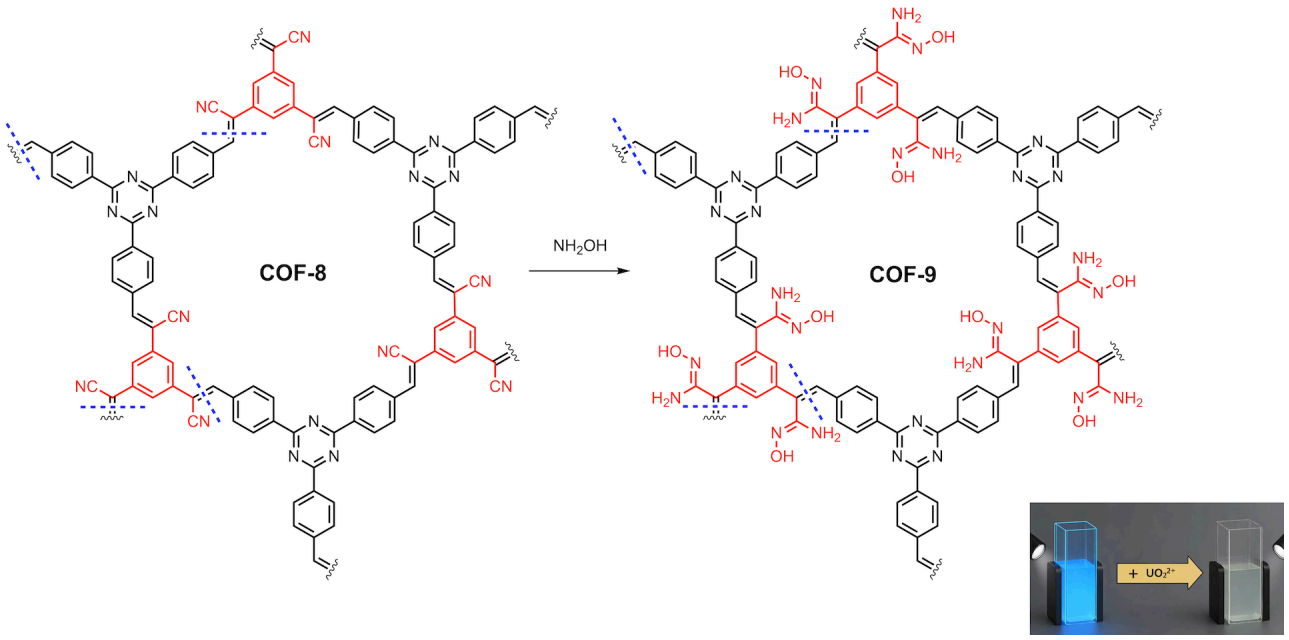
Interaction geometry	E / kJ mol^{-1}	
		
benzene (X = CH) – benzene (b-b)	−7.9	−12.6
benzene-triazine (X = N) (b-t)	−49.8	−55.6
triazine–triazine (t-t)	−6.7	−16.7

COF-8, synthesised from (**E1** + **D2**), is notable for its remarkable stability. The **AA'** slightly shifted mode of a **COF-8** bilayer has a π-π stacking interaction energy of –67.1 kJ mol^{-1} between two layers of one repeat unit.



3.6	**Calculate** the π-π stacking energy between two layers of one repeat unit of **COF-8**, for the **AA**, **AB** and **AB'** arrangements. **Assume** π-π stacking happens only between aromatic units.	12.0 pt

COF-9, obtained from **COF-8**, absorbs UO_2^{2+} ions and loses its fluorescence. In an experiment, a suspension of 5.000 mg **COF-9** in 19.90 $mg\ dm^{-3}$ UO_2^{2+} solution (200.0 mL) was filtered after equilibrium was reached. The final concentration of UO_2^{2+} was 9.225 $mg\ dm^{-3}$.



3.7	**Calculate** the equilibrium absorption capacity at a given temperature (q_e) in $mg\ g^{-1}$ of **COF-9**. **Indicate** the number of UO_2^{2+} ions absorbed per pore. **Assume** that all uranium exists as UO_2^{2+} ions.	5.0 pt