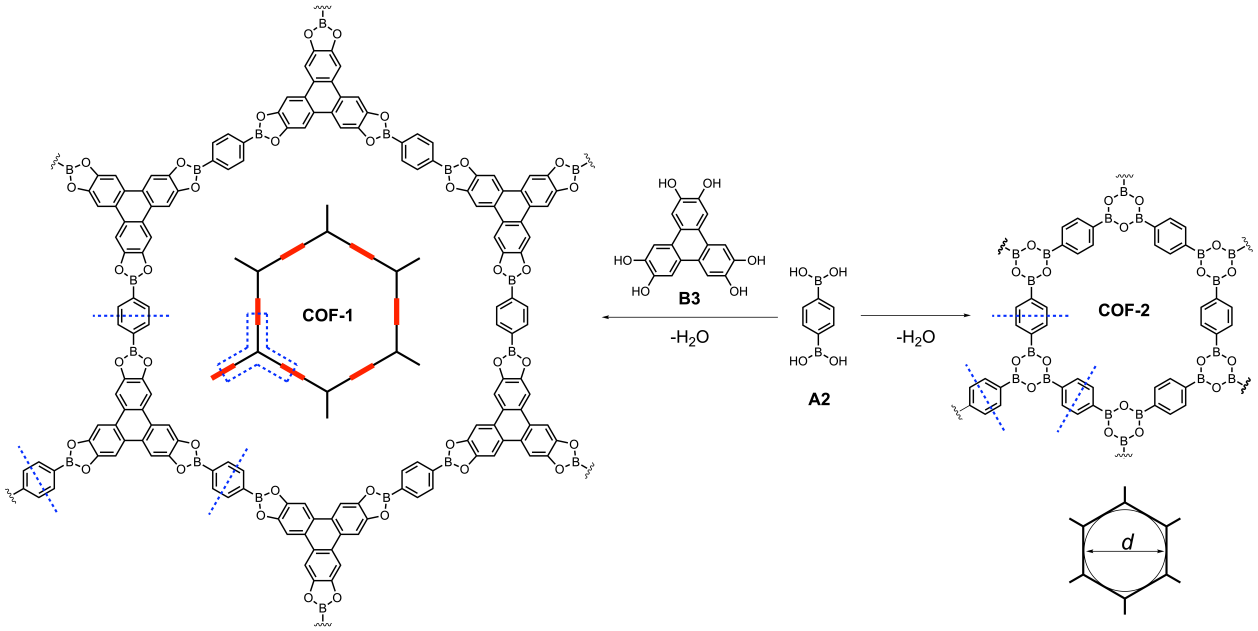
T3. Into Reticular Chemistry

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

SOLUTION:

The empirical formula of **COF-1** is $C_9H_4BO_2$, its elemental composition is

C – $\frac{12.01 \cdot 9}{12.01 \cdot 9 + 4 \cdot 1.008 + 10.81 + 32} \cdot 100\% = 69.77\%$;

C: 69.77%

Empirical formula: $C_9H_4BO_2$

1 pt for empirical formula.

No penalty for $[C_9H_4BO_2]_n$

1 pt for C mass fraction.

no penalty if integer values are used for atomic masses

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.

SOLUTION:

For **COF-2**,

$$a = 2 \cdot B - O + 2 \cdot C - C + 2 \cdot C - B = 8.66$$

$$d = \sqrt{3}a = 15.0$$

$$d = 2r = 15.0$$

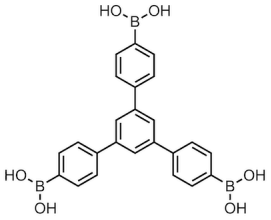
d = 15.0 Å

3 pt for correct d

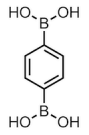
2 pt if only a is given

1 pt if only correct formula is given

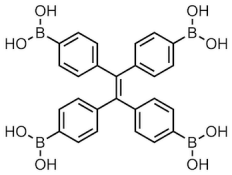
The structures shown below can form 2D and 3D COFs. For this question consider only formation of COFs with boronate esters, imines, and C=C bonds through condensation reactions. **A–E** represent compound classes with different functional groups.



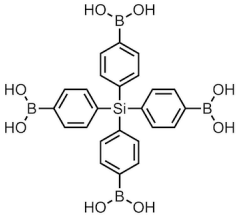
A1



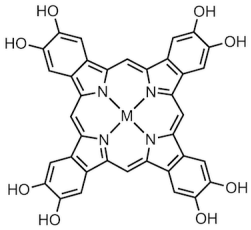
A2



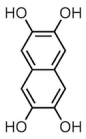
A3



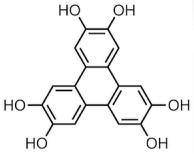
A4



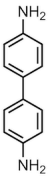
B1



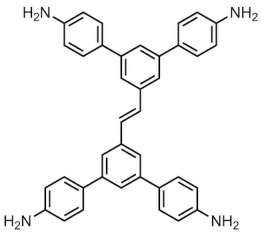
B2



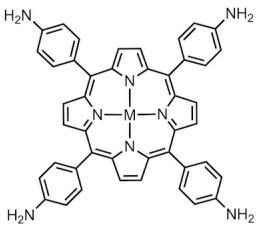
B3



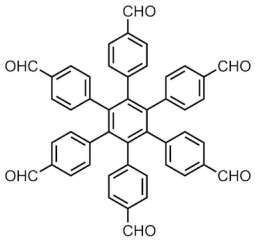
C1



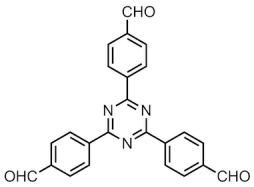
C2



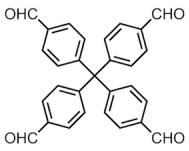
C3



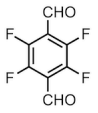
D1



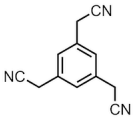
D2



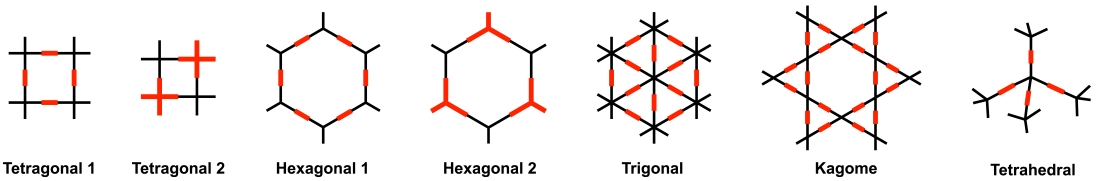
D3



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

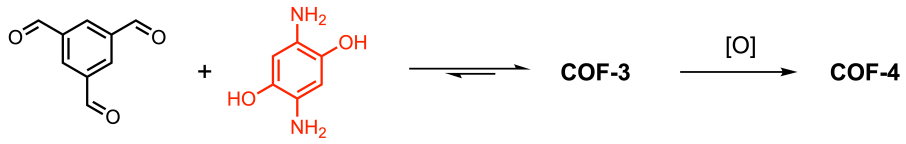
Tetragonal 1	Tetragonal 2	Hexagonal 1	Hexagonal 2	Trigonal	Kagome	Tetra-hedral
		A2 + B3	**E1 + D2**		**C2 + D4**	

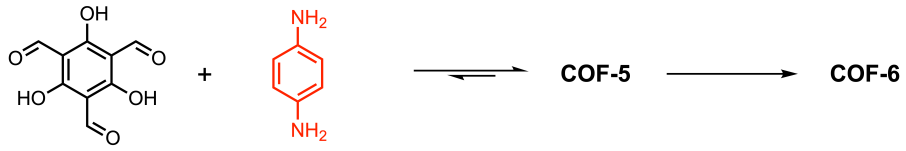
SOLUTION:

Tetragonal 1	Tetragonal 2	Hexagonal 1	Hexagonal 2	Trigonal	Kagome	Tetra-hedral
		A2+B3	**E1+D2**		**C2+D4**	
C3+D4	**XXX**	**A1+B2**	**A1+B3**	**C1+D1**	**A3+B2**	**C1+D3**
A2+B1	**XXX**	**C1+D2**	**XXX**	**XXX**	**XXX**	**A4+B2**

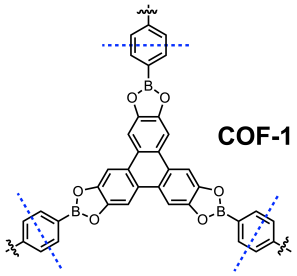
E1 + D4 in *Hexagonal 1* is considered correct
2 pt for correct combination in correct topology
1 pt for XXX in correct topology
-1 pt for incorrect placing of X or combination
0 pt for acetal from the correct combination only
0 pt for blank box

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.

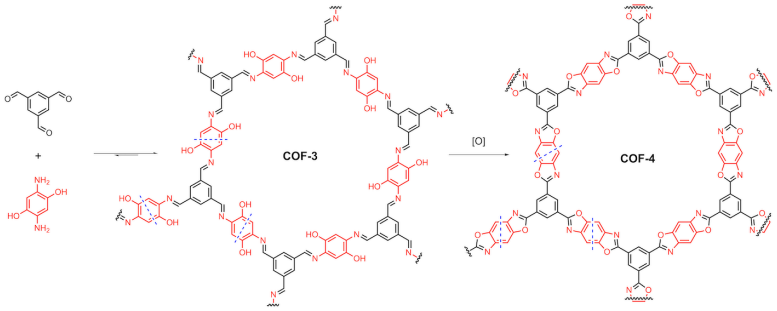

NH2
OH
HO
NH2
COF-3
[O]
COF-4


OH
HO
OH
NH2
NH2
COF-5
COF-6

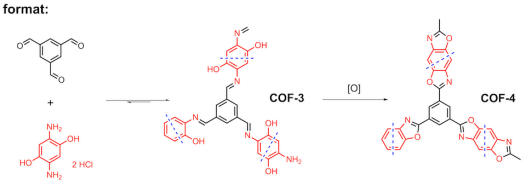
3.4 **Draw** the repeat units for **COFs 3–6.** **Indicate** the edges of each repeat unit with a dashed line as shown for **COF-1** below. 12.0 pt

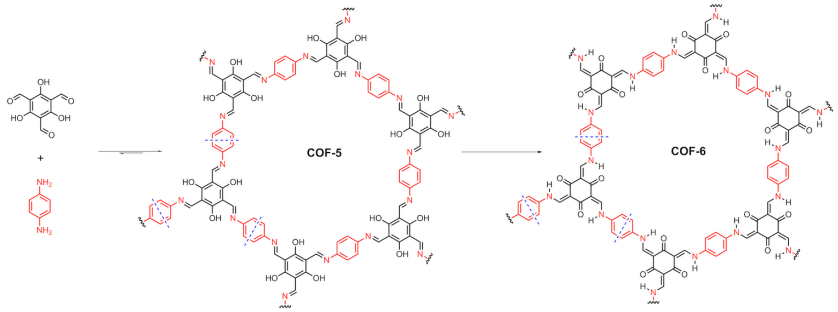


SOLUTION:

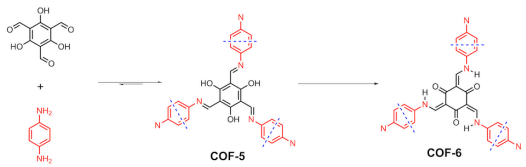


Expected format:



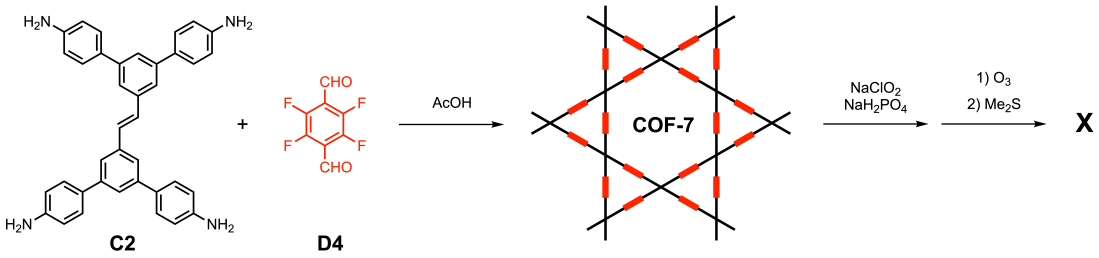


Expected format:



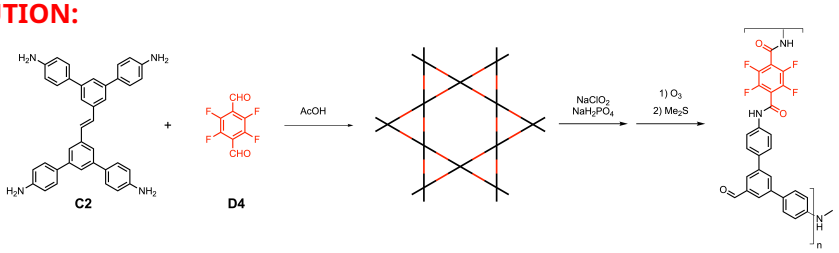
2 pt for each of **COF-3** and **COF-5**. 1 pt for correct structure with wrong defined repeat unit.
4 pt for each of **COF-4** and **COF-6**. 2 pt for correct structure with wrong defined repeat unit.

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



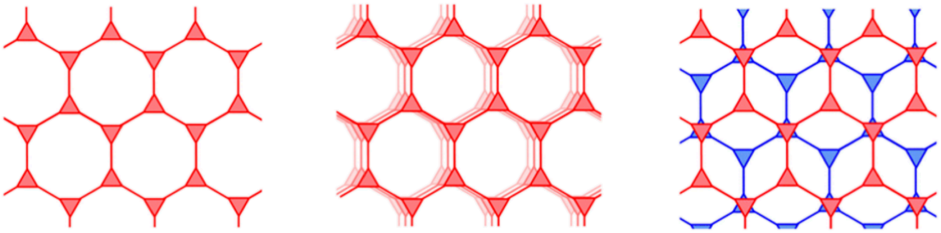
3.5 **Draw** the smallest repeat unit of macrocycle **X**. 6.0 pt

SOLUTION:



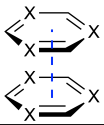
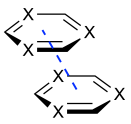
6 pt for repeat unit **X**.
-2 pt for imine product.
-2 pt if aldehyde is not shown.
-2 pt if fluorines are missing.

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

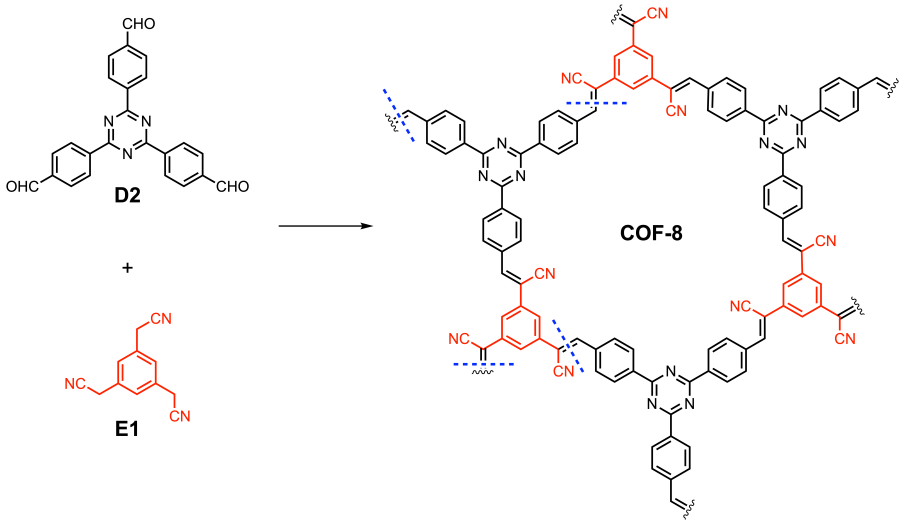


(a) AA (b) AA’ (c) AB

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

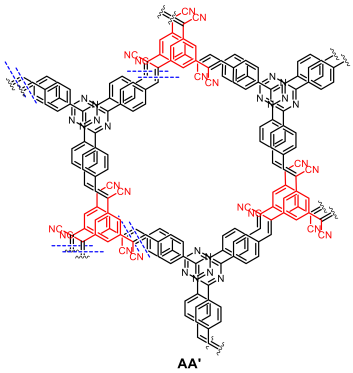
COF-8, synthesised from (**E1 + D2**), is notable for its remarkable stability. The **AA'** slightly shifted mode of a **COF-8** bilayer has a π-π stacking interaction energy of –67.1 kJ mol^{-1} between two layers of one repeat unit.



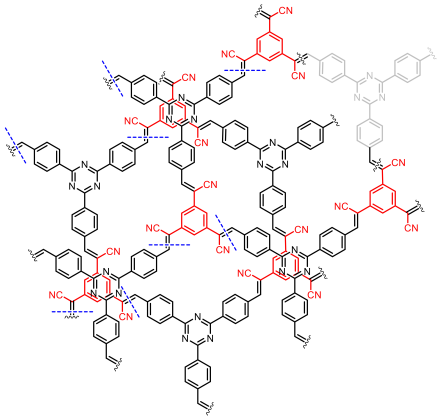
3.6 **Calculate** the π-π stacking energy between two layers of one repeat unit of **COF-8**, for the **AA**, **AB** and **AB'** arrangements. **Assume** π-π stacking happens only between aromatic units. 12.0 pt

SOLUTION:

COF-8 represents hexagonal 2 topology. Each repeat unit contain 4 benzene and 1 triazine rings. For **AA** and **AA'** stacking modes there will be 4 b-b and 1 t-t interactions. For **AB** each repeat unit will have 1 b-t interactions as shown below for **AB'** arrangement (hexagons is redrawn to show all interactions).



AA'



AB'

Thus, calculations will be as follows:

	Interaction number			Interaction energy, $\mathrm{kJ\ mol^{-1}}$			Total energy, $\mathrm{kJ\ mol^{-1}}$
	b-b	b-t	t-t	b-b	b-t	t-t	
AA	4	0	1	−7.9	−49.8	−6.7	−38.3
AA'	4	0	1	−12.6	−55.6	−16.7	−67.1
AB	0	1	0	−7.9	−49.8	−6.7	−49.8
AB'	0	1	0	−12.6	−55.6	−16.7	−55.6

$$AA: 4 \cdot (-7.9) + 1 \cdot (-6.7) = -38.3\ \mathrm{kJ\ mol^{-1}}$$

$$AB: 1 \cdot (-49.8) = -49.8\ \mathrm{kJ\ mol^{-1}}$$

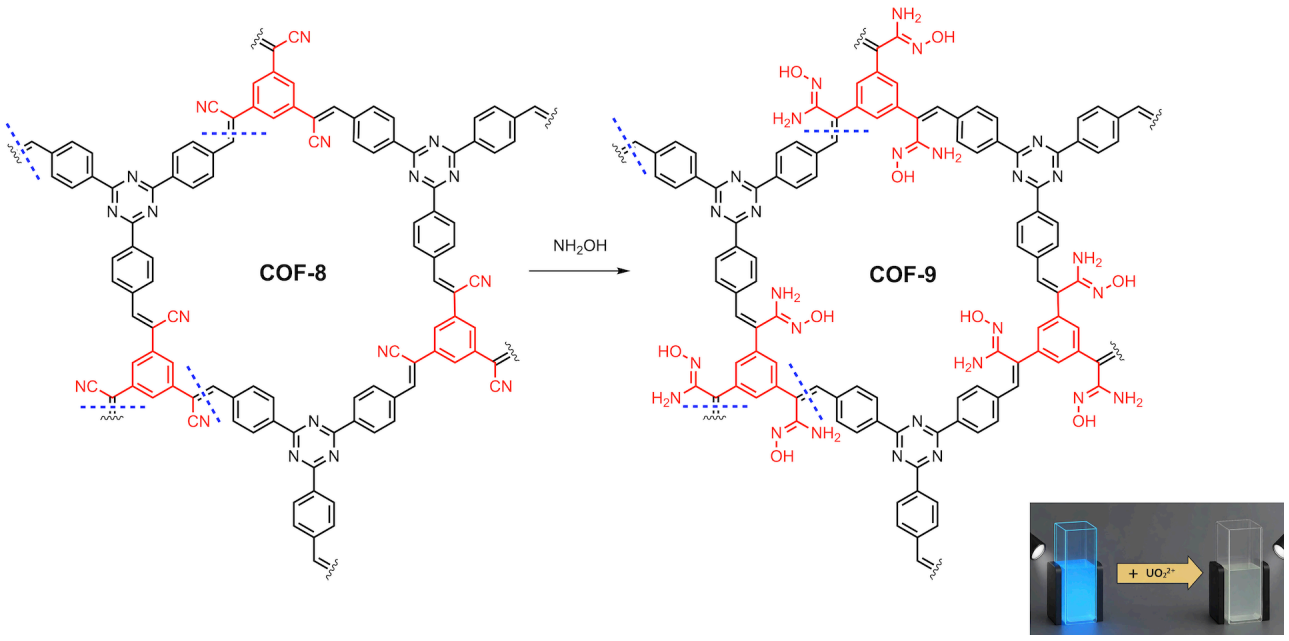
$$AB': 1 \cdot (-55.6) = -55.6\ \mathrm{kJ\ mol^{-1}}$$

(**AB'**) interlayer stacking mode energy matches slipped benzene-triazine π-π stacking.

4 pt for each correct total energy in **AA, AB, AB'**

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 $\mathrm{mg\ dm^{-3}}$ 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

SOLUTION:

$$q_e = \frac{C_0 - C_e}{m \cdot L}$$

$$q_e = \frac{19.90\ mg\ dm^{-3} - 9.225\ mg\ dm^{-3}}{5.000 \cdot 10^{-3}\ g} \cdot 200.0 \cdot 10^{-3}\ dm^3 = 427.0\ mg\ g^{-1}$$

Since one repeating unit ($C_{36}H_{27}N_9O_3$) represents one pore, the molar ratio of the **COF-9** pore to UO_2^{2+}:

$$\frac{1.000g}{633.67g} : \frac{427.0 \cdot 10^{-3}g}{270.03g} = 1 : 1$$

COF-9 pore : UO_2^{2+} = 1:1

2 pt for q_e.

3 pt for correct molar ratio between pore and uranium.

1 pt if only correct molar mass of repeating unit is given.