

Problem 8 11.1% of total	Question	8.1	8.2	8.3	8.4	8.5	8.6	8.7	8.8	Total
	Points	4	4	3	2	2	1	11	5	54
Question	8.9	8.10	8.11	8.12	8.13	8.14	8.15	8.16		
Points	4	2	2	5	1	1	2	5		

Problem 8: Lighting up the World

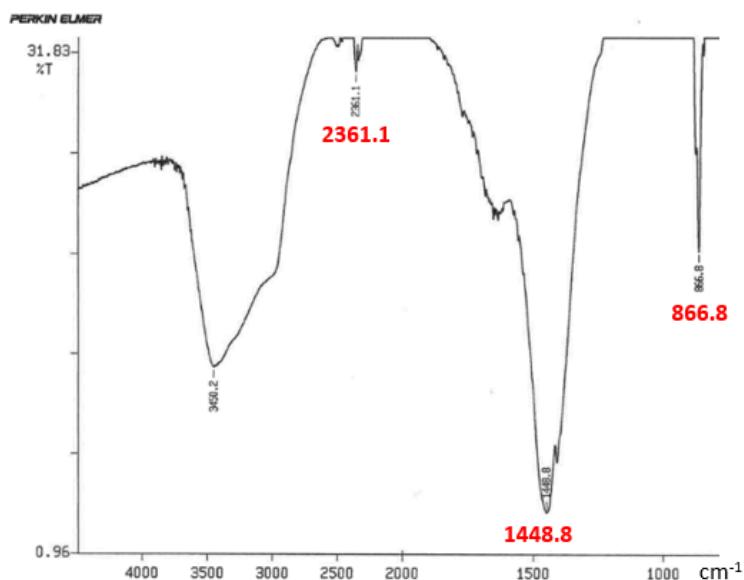
By Lim Dillion, Singapore

Phosphors exhibit luminescence – it emits light when exposed to some type of radiant energy. Currently, new phosphors are being explored for their potential use commercially. Furthermore, some of these are solid-state luminescent sources, which make them of great research interest. In this question, we shall explore two phosphors, both of which revolve around an element **A**.

Part 1: Luminescence properties of A^{3+} -doped powder phosphors

A phosphor, **B1**, involving element **A** was synthesised by Jeong *et al.* in 2010 through a very common way of making luminescent phosphors: doping compounds with certain elements. Phosphor **B1** was synthesised by first weighing a ternary compound **B2**, and three binary compounds **B3**, **B4** and **B5** in stoichiometric ratios, then sintering in air for 4 hours at temperatures from 500 to 800°C.

Consider the infra-red spectrum of compound **B2**:



You may ignore the peak at 3450.2 cm^{-1} . It arises from the O-H stretch of water. On strong heating, the peak at 2361.1 cm^{-1} intensifies.

- 8.1) By considering the peaks highlighted in red, and by knowing that **B2** contains only one metal element with percentage by mass of the metal being between 41 to 45% (ignoring water), determine the identity of **B2**. Show your working clearly. In your formula, you may ignore water contributing to the peak at 3450.2 cm⁻¹.

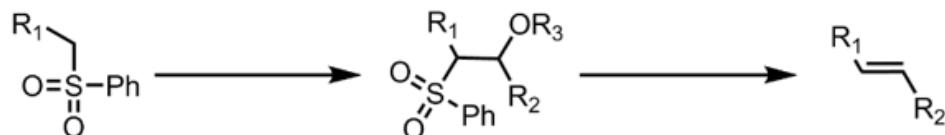
Compound **B3** contains 79.3% by mass of an element. Compound **B4** is strongly basic, reacting readily with CO₂ to give a compound with the same anion as compound **B2**. It has a total molar mass between 355 g mol⁻¹ and 365 g mol⁻¹. Compound **B5** contains element **A**. It is formed by burning element **A** in air above 150°C.

Element **A** has a readily accessible +2 and +3 oxidation state, being one of the few elements in its period to exhibit this property. Compound **A** reacts readily with I₂, and upon being heated, it forms compound **A1**. Compound **A1** is a very useful reagent in organic chemistry, with some of its uses highlighted below:

- Deprotection of *N*-tosylamides



- Julia Olefinations



- Barbier reactions



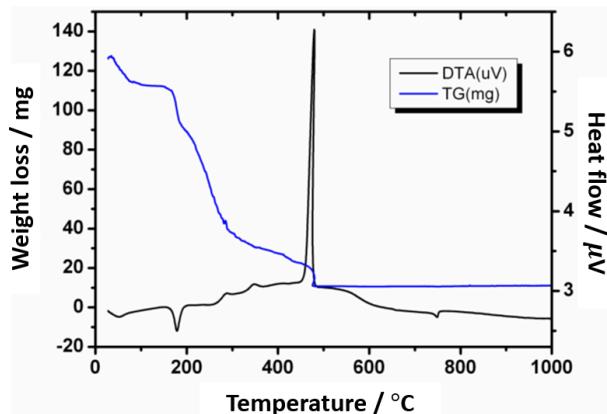
- 8.2) Deduce compounds **B3** and **B4**.

- 8.3) Deduce element **A**, and hence deduce compounds **A1** and **B5**.

As phosphors are usually non-stoichiometric, the structure of **B1** is **PQ_{1-x}R_xS_y**, where **P**, **Q** and **R** are the cations in compounds **B2**, **B4** and **B5**, and **S** is an anion derived from compound **B3**. It is known that 0 < x < 1, and y is an integer.

- 8.4) Deduce phosphor **B1**, leaving the unknown stoichiometric coefficients 1-x and x as written above.

The TG-DTA (thermogravimetric-differential thermal analysis) curves of the phosphor and its precursors is shown below. The TG curve shows how the weight of the phosphor or its precursors change with temperature. While doing DTA, the phosphor and its precursors, and an inert reference were had identical heat flows supplied, and any temperature difference between the sample and reference is recorded. The differential temperature is then plotted against temperature, forming a DTA thermogram.



- 8.5) From the TG curve (blue), **state** the molecule contributing to the loss of mass from 0 to 200°C. **Explain** how the peak at 180°C in the DTA curve (black) corresponds to it.
- 8.6) **State** the temperature at which phosphor **B1** was formed. Justify your answer using data from the TG-DTA curves.

Part 2: Synthesis, crystal structure and luminescence properties of A-containing powder phosphors

Phosphor **C1** is prepared using **B2**, **B4** and **B5**, as well as binary compound **C2**, and ternary compounds **C3**, **C4** and a compound with 4 elements, **C5**.

Compound **C2** is often used for desilylation, and has the same cation as compound **B2**. Compound **C3** exhibits a characteristic green flame, and turns blue litmus paper red. Compound **C4** is often used as a base in organic chemistry due to its solubility in certain organic solvents like alcohols and DMF. Compound **C4** is often used in reactions like the Suzuki and Heck reactions. Compound **C4** has the same anion as compound **B2**.

Compound **C5** consists of 2 polyatomic ions. Compound **C5** can be synthesised by the reaction of a binary compound **C6** and ternary compound **C7**, with compound **C6** deprotonating compound **C7** only once (Reaction I). Compound **C6** reacts with HgCl_2 to form a highly insoluble solid in the Calomel Reaction (Reaction II), which upon addition of KOH, yielded Millon's Base. Compound **C7** is a triprotic acid that readily undergoes condensation with the elimination of water when concentrated (Reaction III), forming a reagent that is often used in organic chemistry for the cyclisation or acylations of compounds, with the alternative being Eaton's reagent.

- 8.7) **Deduce** compounds **C2** to **C7**. Hence, **write** the **balanced** equations for reactions I to III.

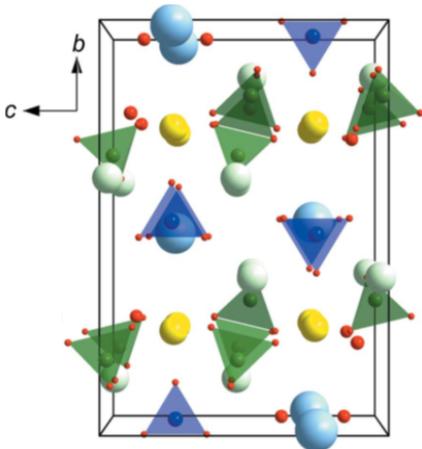
In particular, the phosphor **C1** with the ratio $\mathbf{A}_a\mathbf{B}_b\mathbf{C}_c\mathbf{D}_d\mathbf{E}_e\mathbf{F}_f$, where **A** to **F** are ions from the salts above, is of interest for its luminescent properties. It is known to have the following properties:

- $ab = 2$, $b - (c + d) = 0$, $cd = 0.0784$, $c > d$ and $e < f$.
- All variables from *a* to *f* are rational numbers.
- **B**, **C** and **D** are derived from some of the salts from **B2**, **B4** and **B5**.
- **A** is derived from **C4**.
- **E** and **F** have the same charge.

8.8) **Deduce** the formula of **C1**.

8.9) It is given that the unit cell of **C1** is that shown on the right. By deducing which sphere corresponds to which element, **draw** the shapes that each of the following coordination environment within the unit cell forms:

- **A** coordinating with 0.
- **B** coordinating with 0.
- **D** coordinating with 0.



When the concentration of \mathbf{A}^{3+} is greater than 2%, the emission intensity decreases due to something known as the *concentration quenching effect*. It is well known that concentration quenching is usually caused by the nonradiative energy transfer among \mathbf{A}^{3+} activators due to electric multipolar interactions.

The multipolar interaction type can be determined by the following equation:

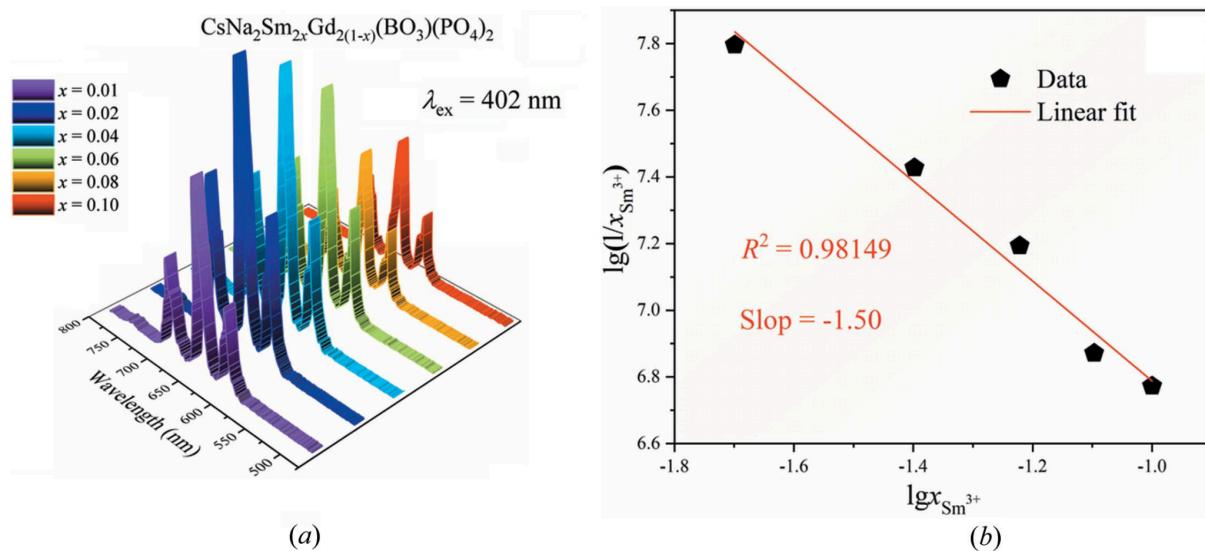
$$\frac{I}{x} = k \left[1 + \beta x^{\frac{\theta}{3}} \right]^{-1}$$

where *I* is the emission intensity at the current concentration, *x* is the \mathbf{A}^{3+} concentration and the values of *k* and β are constants. The constant determines the type of electric multipolar interaction, where $\theta = 6, 8$ and 10 refer to dipole-dipole (d-d), dipole-quadrupole (d-q) and quadrupole-quadrupole (q-q) interactions, respectively.

$$\lg \left(\frac{I}{x} \right) = K - \frac{\theta}{3} \lg x$$

8.10) **Show** that the equation above can be linearised to the form if $\beta x^{\theta/3} \gg 1$, where *K* is a constant to be determined.

The emissions spectrum was then prepared, and the graph above was plotted as shown below:



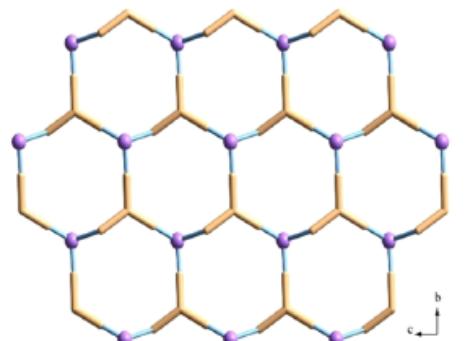
- 8.11) Hence, compute the value of θ and determine the main cause of the quenching mechanism.

Part 3: Metal-Organic Frameworks Involving Ion A for Detection of Quinolinic Acid

Quinolinic acid is an index for some diseases, whose detection is of importance. Elevated quinolinic acid levels are often associated with some diseases like renal cell carcinoma (RCC). The normal quinolinic acid level in human urine is $49 \mu\text{M}$. A study by Zhang *et al.* in 2023 revealed that **A**-metal-organic frameworks containing a ligand **G** can detect quinolinic acid based on its fluorescence emissions.

The ligand **G** is a μ_3 ligand, with one functional group being in a monodentate coordination mode and two identical functional groups being in bidentate coordination modes. The fully protonated form of ligand **G** has a molecular mass of $246.197 \text{ g mol}^{-1}$. The fully protonated form of ligand **G** can be synthesised in 2 steps, starting from meta-xylene (Reaction **IV**).

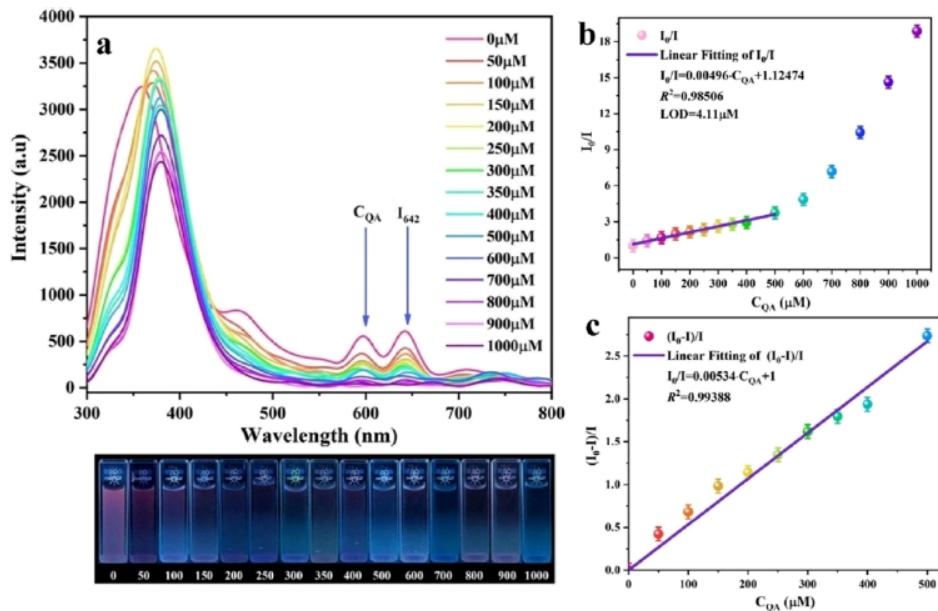
It is known that ligand **G** promotes a 2-dimensional polymerisation, forming a $(3, 6)$ topological network as shown below, consisting of n -membered rings, before the formation of a 3-dimensional supramolecular framework between 2-dimensional layers.



2-dimensional $(3,6)$ topological network

- 8.12) **Deduce** the ligand **G**, and therefore **draw** a monomer of the metal-organic framework which consists of a single A^{n+} ion. **Write down** the two-step reaction scheme for synthesis of the fully protonated form of ligand **G** (reaction **IV**).
- 8.13) **State** the number of atoms in a ring, n , in the (3,6) topological network above.
- 8.14) **State** the intermolecular force leading to the 3-dimensional supramolecular framework for the metal-organic framework.

Its detection capabilities were then examined. The intensity of emissions were recorded as the concentration of quinolinic acid was varied from $0 \mu\text{mol dm}^{-3}$ to $1000 \mu\text{mol dm}^{-3}$.



- (a) Emission spectra of **A**-metal-organic framework suspensions depending as concentration of quinolinic acid was varied from 0 to $1000 \mu\text{M}$, with their photos taken under a 254 nm UV light;
 (b) the plot of I_0/I vs concentration of quinolinic acid from $0-1000 \mu\text{M}$; and
 (c) the plot of $(I_0 - I)/I$ vs concentration of quinolinic acid from $50-500 \mu\text{M}$.

- 8.15) **Explain** briefly why an increase in the concentration of quinolinic acid leads to an increase in the ratio I_0/I .

The linear regression equation obtained was $I_0/I = 0.00496 \cdot C_{\text{QA}} + 1.12474$. To test out this new detection method, some people suspected of RCC had their urine samples tested. 1 mg of **A**-metal-organic framework was dispersed into 3 mL of deionized water with a 2 minute ultrasonic vibration, before being poured into the urine samples, and then these samples were spectrophotometrically tested. The results are shown below.

Patient number	1	2	3	4	5
Volume of urine / mm^3	21754	530	2150	38128	170
Absorbance recorded / Abs	0.124	0.118	0.083	0.129	0.056

- 8.16) **State**, with justification, which patient(s) are likely to have RCC based on the data above. **Calculate** the quinolinic acid concentration in their urine sample(s).

Problem 8: Solution

- 8.1) By considering the peaks highlighted in red, and by knowing that **B2** contains only one metal element with percentage by mass of the metal being between 41 to 45% (ignoring water), **determine** the identity of **B2**. Show your working clearly. In your formula, you may ignore water contributing to the peak at 3450.2 cm⁻¹.

B2 is likely ionic from the information in the question.

The peak at 2361.1 cm⁻¹ is likely to be a C-O stretch of CO₂.

The peak at 1448.8 cm⁻¹ is likely to be the C-O stretch of CO₃²⁻.

The peak at 866.8 cm⁻¹ is likely to be the C-O bending modes of CO₃²⁻.

Hence, **B2** is likely a carbonate.

Let **B2** be M_xCO₃. Let A_r(M) = m.

Thus,

$$0.41 \leq \frac{xm}{xm+12+16\times 3} \leq 0.45 \Rightarrow 0.41xm + 24.6 \leq xm \text{ and } xm \leq 0.45xm + 27$$

We can further rearrange this to:

$$\frac{24.6}{1-0.41} \leq xm \leq \frac{27}{1-0.45} \Rightarrow 41.69 \leq xm \leq 49.09$$

If x = 1, 41.69 ≤ m ≤ 49.09. The only element corresponding to this is Ti, and the compound is TiCO₃. Ti²⁺ is not very common, so unlikely to be Ti.

If x = 2, 20.85 ≤ m ≤ 24.55. The only element corresponding to this is Na, and the compound is Na₂CO₃. Hence, it is likely to be Na.

B2 is Na₂CO₃.

1 point for determining CO₃²⁻ anion using IR data.

1 point for justifying Na⁺ cation using mass data.

2 points for correct B2.

8.2) **Deduce** compounds **B3** and **B4**.

For **B3**, let **M** be the metal. Let the $A_r(\mathbf{M}) = m$.

79.3% is likely to be the metal, which judging from the percent mass, is likely to be very heavy. Then, we consider various common counterions, like O^{2-} , Cl^- and so on.

$$\text{Let } \mathbf{B3} \text{ be } \mathbf{MO}_x. \text{ Then } \frac{m}{m + 16x} = 0.793 \Rightarrow m = 61.29x$$

x	m	Possible metals
1	61.29	No metals correspond
2	122.58	No metals correspond
3	183.87	Likely W, and WO_3 makes sense

Beyond this, masses are too high to be likely.

$$\text{Let } \mathbf{B3} \text{ be } \mathbf{MF}_x. \text{ Then } \frac{m}{m + 19x} = 0.793 \Rightarrow m = 72.787x$$

x	m	Possible metals
1	72.787	Ge, but GeF is very unlikely to exist
2	145.574	Maybe Pm, but it only shows one stable oxidation state of +3

Beyond this, masses are too high to be likely.

$$\text{Let } \mathbf{B3} \text{ be } \mathbf{MCl}_x. \text{ Then } \frac{m}{m + 35.5x} = 0.793 \Rightarrow m = 136x$$

x	m	Possible metals
1	135.997	No metals correspond
2	271.994	No metals correspond

Beyond this, masses are too high to be likely.

For halides beyond Cl, notice that written in the form $m = ax$, a will only get larger and larger. For Br, $a = 306.1$ and so on, so it cannot be a bromide, iodide, etc.

Hence, **B3** is WO_3 .

Since **B4** is strongly basic, it is likely a metal oxide.

It has a molar mass between 355 and 365 g mol⁻¹.

Let it be $\mathbf{M}_x\mathbf{O}_y$.

If $y = 1$, $x A_r(\mathbf{M}) = 339$ to 349 g mol⁻¹. If $x = 1$, we do not have any plausible candidates. If $x = 2$, we get some of the *f*-block metals, unlikely in this case to exhibit the +1 oxidation state.

If $y = 2$, $x A_r(\mathbf{M}) = 323$ to 333 g mol⁻¹. If $x = 1$, we again do not have any plausible candidates. If $x = 2$, it reduces to the case of $\mathbf{M}_2\mathbf{O}_2$, which is simply \mathbf{MO} , so not possible.

If $y = 3$, $x A_r(\mathbf{M}) = 307$ to 317 g mol⁻¹. If $x = 1$, we again do not have any plausible candidates. If $x = 2$, we find that the only possible \mathbf{M} is Gd. $\mathbf{Gd}_2\mathbf{O}_3$ is possible.

Hence, **B4** is $\mathbf{Gd}_2\mathbf{O}_3$.

1 point for considering a few anions for B3, and deducing that oxide must be the anion.

1 point for deducing B3 as \mathbf{WO}_3 .

1 point for trying out various values of y as shown above.

1 point for deducing B4 as $\mathbf{Gd}_2\mathbf{O}_3$.

8.3) **Deduce** element **A**, and hence **deduce** compounds **A1** and **B5**.

By considering the organic reactions, compound **A1** is likely \mathbf{SmI}_2 .

Hence, element **A** is Sm.

Burning Sm in air is likely to give $\mathbf{Sm}_2\mathbf{O}_3$, which is compound **B5**.

1 point for each correct compound and element.

8.4) **Deduce** phosphor **B1**, leaving the unknown stoichiometric coefficients $1-x$ and x as written above.

We know that phosphor **B1** has the form $\mathbf{PQ}_{1-x}\mathbf{R}_x\mathbf{S}_y$. **P** is Na, **Q** is Gd, **R** is Sm.

Gd and Sm have oxidation state 3+, so **S_y** should have an overall charge of 4-.

Since **S** is associated with \mathbf{WO}_3 , the corresponding anion should be \mathbf{WO}_4^{2-} .

Thus, **B1** should be $\mathbf{NaGd}_{1-x}\mathbf{Sm}_x(\mathbf{WO}_4)_2$.

1 point for identifying the correct anion, 1 point for correct B1.

- 8.5) From the TG curve (blue), **state** the molecule contributing to the loss of mass from 0 to 200°C. **Explain** how the peak at 180°C in the DTA curve (black) corresponds to it.

At such low temperatures, it is likely to be water of crystallisation, as seen in the IR spectrum of Na_2CO_3 at the very start. Hence, the molecule is likely to be H_2O .

The DTA shows a dip, corresponding to an endothermic process. Loss of water of crystallisation is an endothermic process.

1 point for identifying the correct molecule, 1 point for correct identification of the endothermic process.

- 8.6) **State** the temperature at which phosphor **B1** was formed. Justify your answer using data from the TG-DTA curves.

475°C, where the sharp peak was shown, corresponding to a very exothermic reaction which was phosphor formation (bond forming is an exothermic process).

1 point for any temperature between 450°C to 500°C, justifying using the peak.

- 8.7) **Deduce** compounds **C2** to **C7**. Hence, **write** the **balanced** equations for reactions I to III.

Compound **C2** is often used for desilylation, and has the same cation as compound **B2**. Hence, compound **C2** has a fluoride anion, so **C2** is NaF.

Compound **C3** exhibits a characteristic green flame, and turns blue litmus paper red. Compound **C3** is clearly H₃BO₃.

Compound **C4** is often used as a base in organic chemistry due to its solubility in certain organic solvents like alcohols and DMF. Compound **C4** is often used in reactions like the Suzuki and Heck reactions. Compound **C4** has the same anion as compound **B2**.

Compound **C4** is Cs₂CO₃.

Compound **C6** reacts with HgCl₂ to form a highly insoluble solid in the Calomel Reaction, which upon addition of KOH, yielded Millon's Base.

Compound **C6** must be NH₃, because HgCl₂ + NH₃ → HgCl(NH)₂ (highly insoluble) + NH₄Cl. Upon addition of base, it forms Hg₂(OH)N·xH₂O, which is Millon's Base.

Compound **C7** is a triprotic acid that readily undergoes condensation with the elimination of water when concentrated, forming a reagent that is often used in organic chemistry for the cyclisation or acylations of compounds, with the alternative being Eaton's reagent.

The reagent mentioned in the end of the question is polyphosphoric acid (PPA). Hence, compound **C7** must be H₃PO₄.

Compound **C5** consists of 2 polyatomic ions. Compound **C5** can be synthesised by the reaction of a binary compound **C6** and ternary compound **C7**, with compound **C6** deprotonating compound **C7** only once.

H₃PO₄ reacting with NH₃ in the correct stoichiometric ratio yields **C5** being NH₄H₂PO₄.

Reaction I: NH₃ + H₃PO₄ → NH₄H₂PO₄.

Reaction II: HgCl₂ + 2NH₃ → HgCl(NH)₂ + NH₄Cl.

Reaction III: n H₃PO₄ → HO(−P(O)(OH)−O−)_nH + (n−1) H₂O.

1 point for each correct answer.

1 point for reaction I, 2 points for reactions II and III.

If unbalanced, deduct 0.5 points.

If wrong products, 0 points.

For reaction I, if (NH₄)₂HPO₄ or (NH₄)₃PO₄ is given, give 0.5 points.

For reaction III, if lower polyphosphoric acids like H₄P₂O₇, give 0.5 points.

8.8) **Deduce** the formula of **C1**.

Since $b - (c + d) = 0$ and $cd = 0.0784$, and we know that **A** must be Cs, and since c and d are fractional, we know that **B** must be Na. Correspondingly, **C** and **D** should correspond to Gd and Sm as in part 1.

Hence, we can guess that **E** and **F** must correspond to H_3BO_3 and $\text{NH}_4\text{H}_2\text{PO}_4$. It is likely that these give rise to anions. **E** likely gives rise to BO_3^{3-} and **F** therefore gives rise to PO_4^{3-} , since both **E** and **F** have the same charge.

Thus, we know that $a + b + 3(c+d) - 3e - mf = 0$.

Since $b = c + d$, this simplifies to $a + 4b - 3e - mf = 0$.

Since $ab = 2$, we can guess that either $a = 1, b = 2$ or $a = 2, b = 1$.

If $a = 2, b = 1$, that means that $cd = 0.0784$, $c + d = 1$. Solving this system of equations, we realise that c and d have surds in them, and are hence not rational.

Thus, $a = 1, b = 2$, and $(c, d) = (1.96, 0.04)$. We know that Sm is doped, hence Sm corresponds to d while Gd corresponds to c .

Hence, $1 + 4 \times 2 - 3e - 3f = 0$.

If $e = 1, 3f = 6, f = 2$.

If $e = 2, 3f = 3$. Knowing that $e < f$, this cannot be the case.

Hence, **C1** must be $\text{CsNa}_2\text{Gd}_{1.96}\text{Sm}_{0.04}(\text{BO}_3)(\text{PO}_4)_2$.

1 point for all correct elements and ions.

1 point for correct subscripts for Cs, Na.

1 point for correct subscripts for Gd, Sm.

1 point for correct subscripts for BO_3^{3-} and PO_4^{3-} .

1 point for the correct formula for C1.

- 8.9) It is given that the unit cell of **C1** is that shown on the right. By deducing which sphere corresponds to which element, **draw** the shapes that each of the following coordination environment within the unit cell forms:

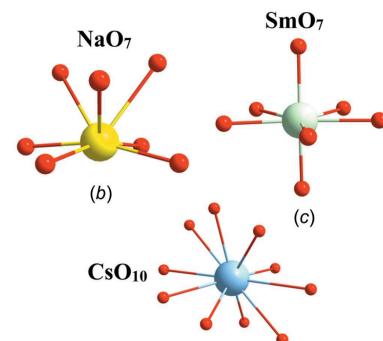
- **A** coordinating with O.
- **B** coordinating with O.
- **D** coordinating with O.

Consider the following environments on the right:

- NaO_7 forms a truncated square pyramid.
- Each Sm^{3+} cation is also coordinated by seven O atoms to form an SmO_7 pentagonal bipyramidal.
- Cs^+ connects to 10 O atoms to form a polyhedra.

2 points for correct geometry of SmO_7 environments.

1 point each for the correct number of atoms of NaO_7 and CsO_{10} environments.



$$\lg\left(\frac{I}{x}\right) = K - \frac{\theta}{3} \lg x$$

- 8.10) **Show** that the equation above can be linearised to the form if $\beta x^{\theta/3} \gg 1$, where K is a constant to be determined.

$$\begin{aligned}\frac{I}{x} &= k \left[1 + \beta x^{\frac{\theta}{3}} \right]^{-1} \Rightarrow \frac{I}{x} = k \beta^{-1} x^{-\frac{\theta}{3}} \\ \Rightarrow \lg\left(\frac{I}{x}\right) &= \lg k - \lg \beta - \frac{\theta}{3} \lg x \\ \Rightarrow \lg\left(\frac{I}{x}\right) &= K - \frac{\theta}{3} \lg x \quad (K = \lg k - \lg \beta)\end{aligned}$$

0.5 points for the approximation (step 1).

0.5 points for usage of logarithm rules (step 2).

1 point for correct linearisation, with the statement of K .

- 8.11) Hence, **compute** the value of θ and **determine** the main cause of the quenching mechanism.

Since slope = -1.5, $\theta = -3(\text{slope}) = 4.5$. This is closest to 6, implying that the quenching mechanism originates from d-d interactions between Sm³⁺ cations.

1 point for computation of θ .

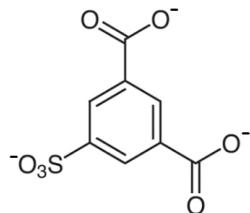
1 point for the correct conclusion that the quenching mechanism originates from d-d interactions.

- 8.12) **Deduce** the ligand **G**, and therefore **draw** a monomer of the metal-organic framework which consists of a single A^{n+} ion. **Write down** the two-step reaction scheme for synthesis of the fully protonated form of ligand **G** (reaction **IV**).

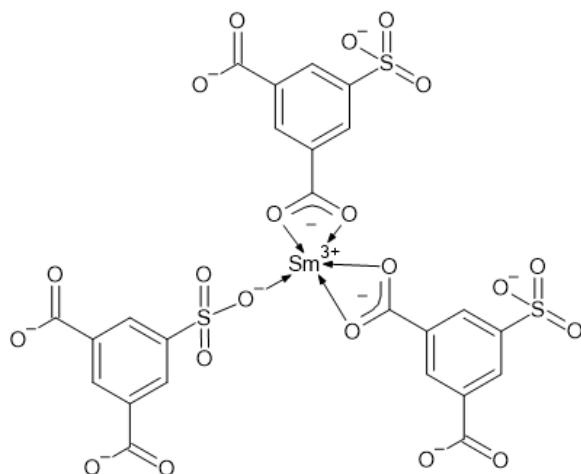
Since ligand **G** can be formed from m-xylene, it is clear that ligand **G** should most likely contain a benzene ring.

Subtracting away the mass of the benzene ring, the remaining molecular mass is $246.197 - 6 \times 12.011 - 6 \times 1.008 = 108.083$. Since ligand **G** is a μ_3 ligand, and two are bidentate, we can guess that two of them are carboxylate groups. The remaining mass is $108.083 - 2 \times (12.011 + 15.999 \times 2 + 1.008) = 78.049$. Trying out various common groups, we find that the last group is most likely a SO_3H group, accounting for the 3 H atoms that were substituted.

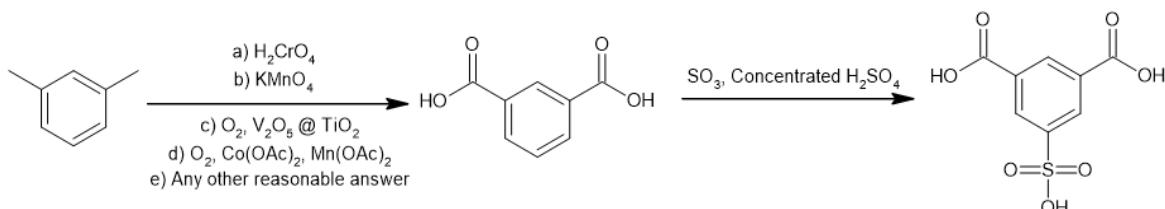
Hence, ligand **G** is the anionic form of 5-sulfoisophthalic acid, or as shown below:



Hence, the monomer will look as follows:



Any reasonable synthesis will be accepted (any condition from a to e will be accepted):



1 point for deducing the carboxylate anion as a ligand of the MOF.

1 point for deducing the structure of **G.**

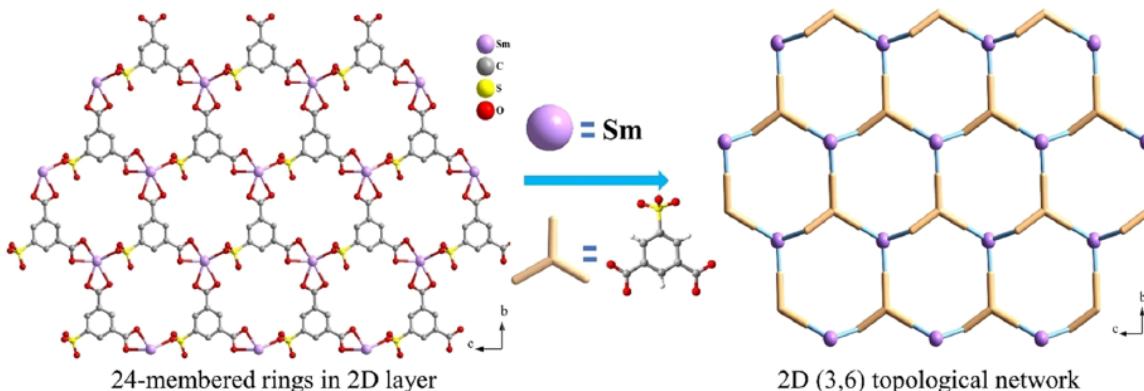
1 point for correct structure of the monomer.

1 point for a reasonable first step for the conversion of m-xylene to isophthalic acid.

1 point for a reasonable second step for the conversion of isophthalic acid to **G.**

- 8.13) **State** the number of atoms in a ring, n , in the (3,6) topological network above.

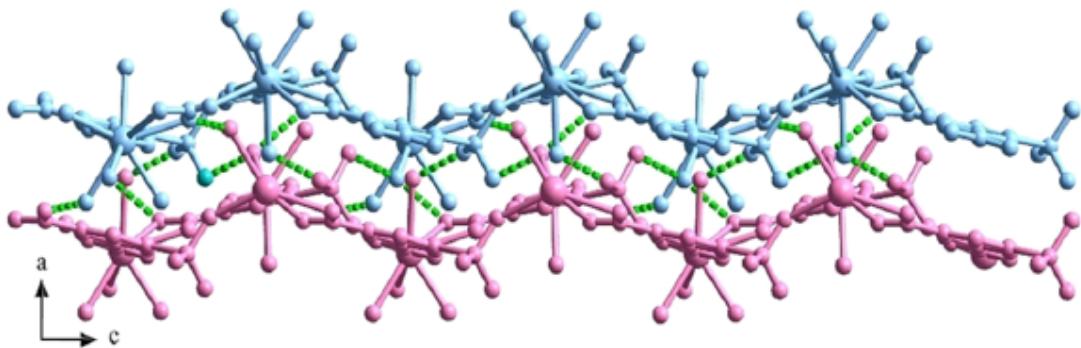
$n = 24$ atoms. See the picture below for a better understanding of why the answer is 24.



1 point for the correct answer.

- 8.14) **State** the intermolecular force leading to the 3-dimensional supramolecular framework for the metal-organic framework.

Hydrogen bonding. The green bonds below are the hydrogen bonds.



1 point for the correct answer.

- 8.15) **Explain** briefly why an increase in the concentration of quinolinic acid leads to an increase in the ratio I_0/I .

Quinolinic acid competes with the SIP^{3-} ligand (5-sulfoisophthalate ion ligand) and blocks the ligand to metal charge-transfer energy transferring path from SIP^{3-} to Sm(III) , thus quenching the ${}^4\text{G}_{5/2} \rightarrow {}^4\text{H}_J$ transitions. This causes a decrease in the intensity of emission, causing I to decrease, and thus I_0/I to increase.

1 point for identifying quinolinic acid competing with the ligand, blocking the LMCT energy transfer and quenching the associated transitions. The specific transition (${}^4\text{G}_{5/2} \rightarrow {}^4\text{H}_J$) need not be identified.

1 point for identifying that this causes a decrease in the intensity of emission, and the ratio is inversely proportional to the intensity of emission.

- 8.16) **State**, with justification, which patient(s) are likely to have RCC based on the data above. **Calculate** the quinolinic acid concentration in their urine sample(s).

Since the normal quinolinic acid level in human urine is 49 μM , we shall compute the quinolinic acid levels in each of the urine samples.

We already have each of the absorbances, and recall that absorbance = $\log_{10}(I_0/I)$. We can hence compute the ratio $I_0/I = 10^{\text{absorbance}}$, and by using the linear regression formula, we can compute the concentration of quinolinic acid in the sample **after the MOF was added**. We can use $[\text{quinolinic acid}] = 201.6129(I_0/I) - 226.7621$.

Patient number	1	2	3	4	5
Volume of urine / mm ³	21754	530	2150	38128	170
Absorbance recorded / Abs	0.124	0.118	0.083	0.129	0.056
I_0/I	1.330	1.312	1.211	1.346	1.138
Concentration of quinolinic acid after MOF added / μM	41.4747	37.7943	17.3101	44.5807	2.5982

Now, all the concentrations look normal, but we need to consider that the sample was **diluted** when we added in the MOF sample. We notice that in the preparation of the final sample, we added 3 mL of the MOF sample. We can therefore obtain the original concentration of quinolinic acid, C_0 from the concentration of quinolinic acid after MOF was added, C_1 through the following relationship: $C_0 = (C_1 \times (V_{\text{urine}} \times 10^{-6} + 3 \times 10^{-3})) / (V_{\text{urine}} \times 10^{-6})$. Now, calculating the original concentration of quinolinic acid for each patient, we obtain:

Patient number	1	2	3	4	5
Volume of urine / mm ³	21754	530	2150	38128	170
Concentration of quinolinic acid after MOF added / μM	41.4747	37.7943	17.3101	44.5807	2.5982
Original concentration of quinolinic acid / μM	47.1943	251.7245	41.4637	48.0884	48.4495

Hence, we see that the only patient with an elevated quinolinic acid level is patient **2**, with a quinolinic acid concentration of 251.7245 $\mu\text{mol dm}^{-3}$ in their urine.

- 1 point for computing the ratio I_0/I using the definition of absorbance for all patients.**
- 1 point for computing the concentration of quinolinic acid using the calibration curve.**
- 1 point for factoring in dilution, and computing the original concentration of quinolinic acid in their urine.**
- 1 point for coming to the conclusion that patient 2 is most likely to have RCC due to elevated quinolinic acid levels.**
- 1 point for correct concentration of quinolinic acid in patient 2's urine.**