

# 'Zinc-ing' to the future: Investigating OLED materials from Zinc PMO's

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## AIMS:

- Preparation of the 'Silylated Zinc Complex' - Zinc 5-choloromethyl-quinolinol with organosilica groups - from literature.<sup>1</sup>
- Attempt synthesis of a potential 100% loaded gel via P123 surfactant and varying EtOH/HCl quantities.
- NMR/TEM Characterisation and fluorometer analysis of the gel product.

## INTRODUCTION:

OLED's – organic light emitting diodes – are fast becoming a staple in technology, due to their colour quality, lack of backlighting, and ability to give curved screens. These diodes work by using an organic emitting layer, *figure 1*, where electrons and holes recombine and give out photons of light whose colour is determined by the band gap of the emitting layers molecules.

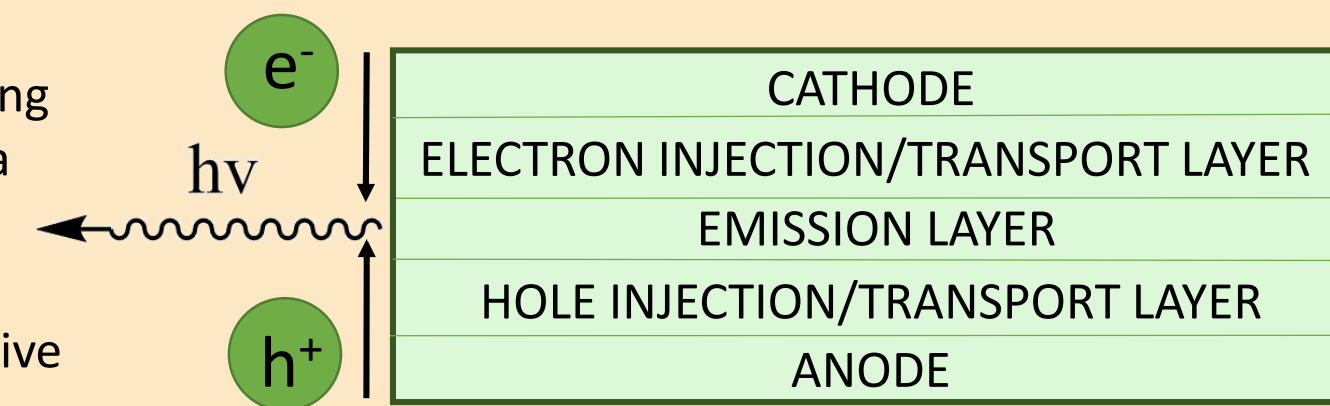


Figure 1: Schematic of an OLED, showing charge recombination.<sup>2</sup>

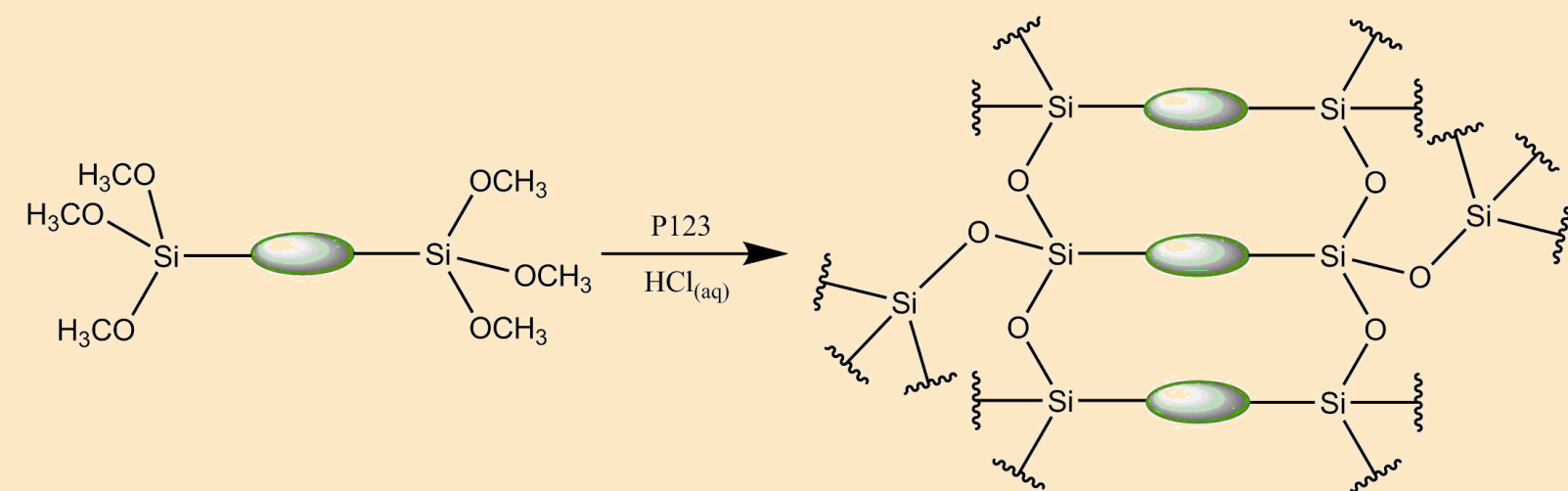
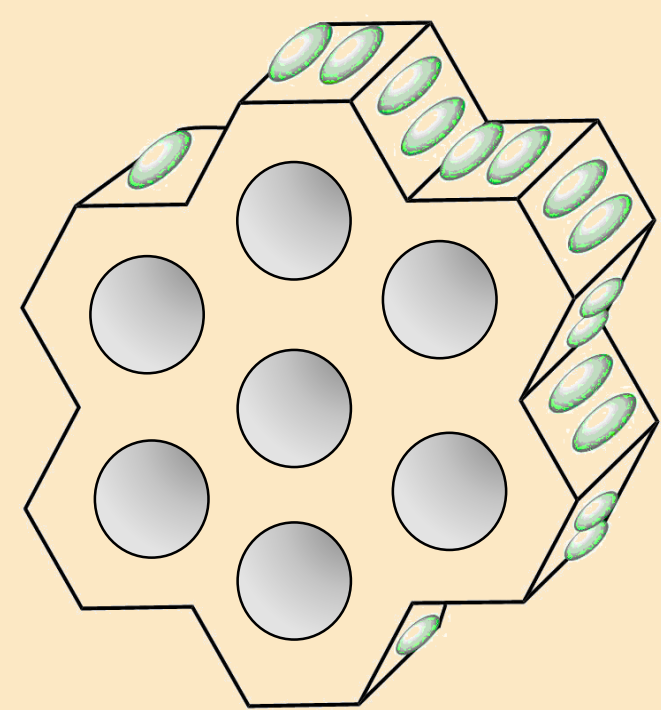


Figure 2: Formation of PMOs from individual units via Si-O bonds via Acid-catalysed hydrolysis (above) to give a porous 3D structure with dye group in the materials walls (Below)



A candidate molecule for this emitting layer is a PMO – Periodic Mesoporous Organosilica; a regularly pored organic polymer containing silica. These PMO's are made via the condensation reaction of many dye-containing molecules with silicon groups that can be reacted to give silicon-oxygen bonds, around a template/surfactant. The pores formed by the linkages allow for a second dye to potentially be added, which can affect the wavelength of light emitted by the PMO when it is excited by photons of a specific wavelength.

## METHOD:

An 8-quinolinol starting material was chloro-methylated with concentrated HCl and formaldehyde to give 5-chloro-8-quinolinol; then this product was reacted with zinc acetate under a nitrogen atmosphere to give a 4-coordinate zinc complex, and finally silylated with MPTMS to allow for polymerisation.

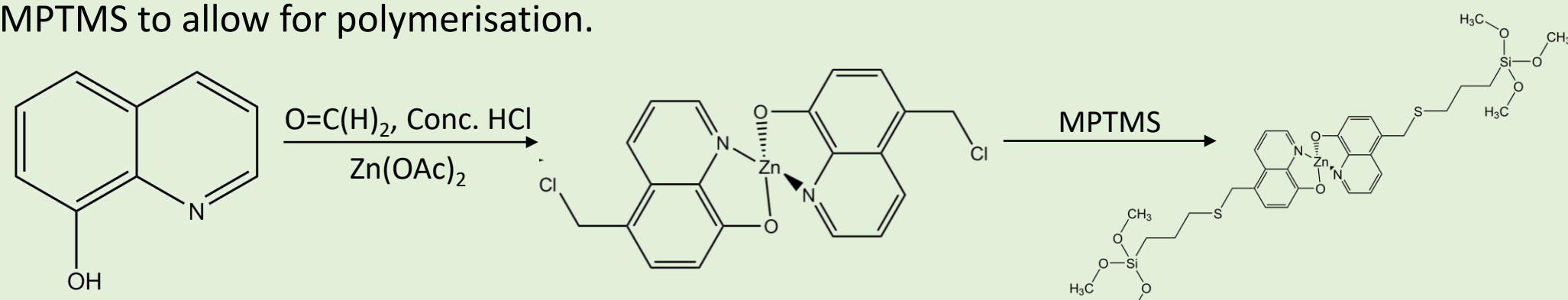


Figure 3: A reaction scheme for the formation of the Silylated Zinc complex from 8-Quinolinol.

## RESULTS:

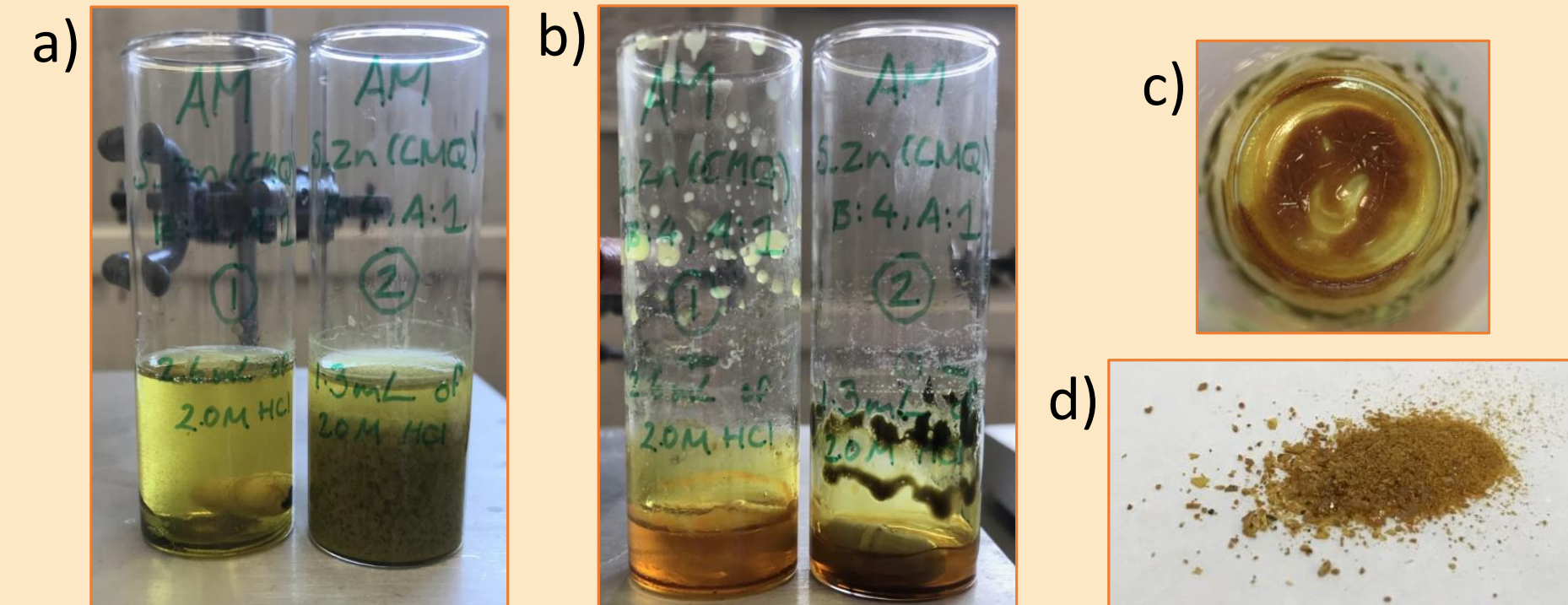


Figure 4: a) Samples directly after addition of 2.6 ml and 1.3 ml of 2.0M HCl respectively, b) samples after evaporation – note the colour change to transparent orange. c + d) Crystalline solid formed after total evaporation of the ethanol/acid solvent.

As shown above in *figures 4a and b*, after the addition of 2.0M HCl and topping up solvent to 10 mL with ethanol, the green suspension of silylated zinc complex in Vial 1 appeared to disintegrate to the bottom of the glass, whilst in Vial 2 it gained a curdled appearance.

As the solvents evaporated, the translucent green colour changed to that of a transparent orange, and the settled silylated zinc complex produced translucent orange crystalline powder – *figures 4c and d*.

A sample of the solvent washings for each vial was withheld, and ran as an excitation spectrum on a F980 Fluorometer. This technique was used to confirm that the hydrochloric acid had not destroyed the Zinc complex as *figure 5* shows. The crystalline powder samples

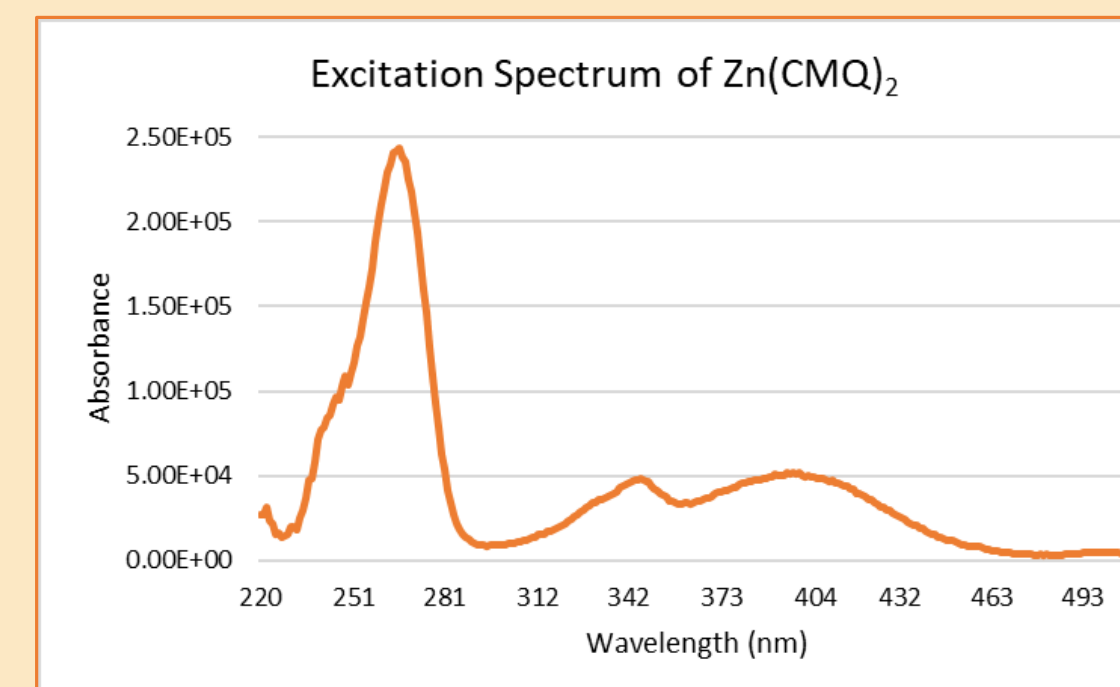


Figure 5: Zinc complex Excitation data, showing the two characteristic bands - from ~232-290nm and 304-370nm.

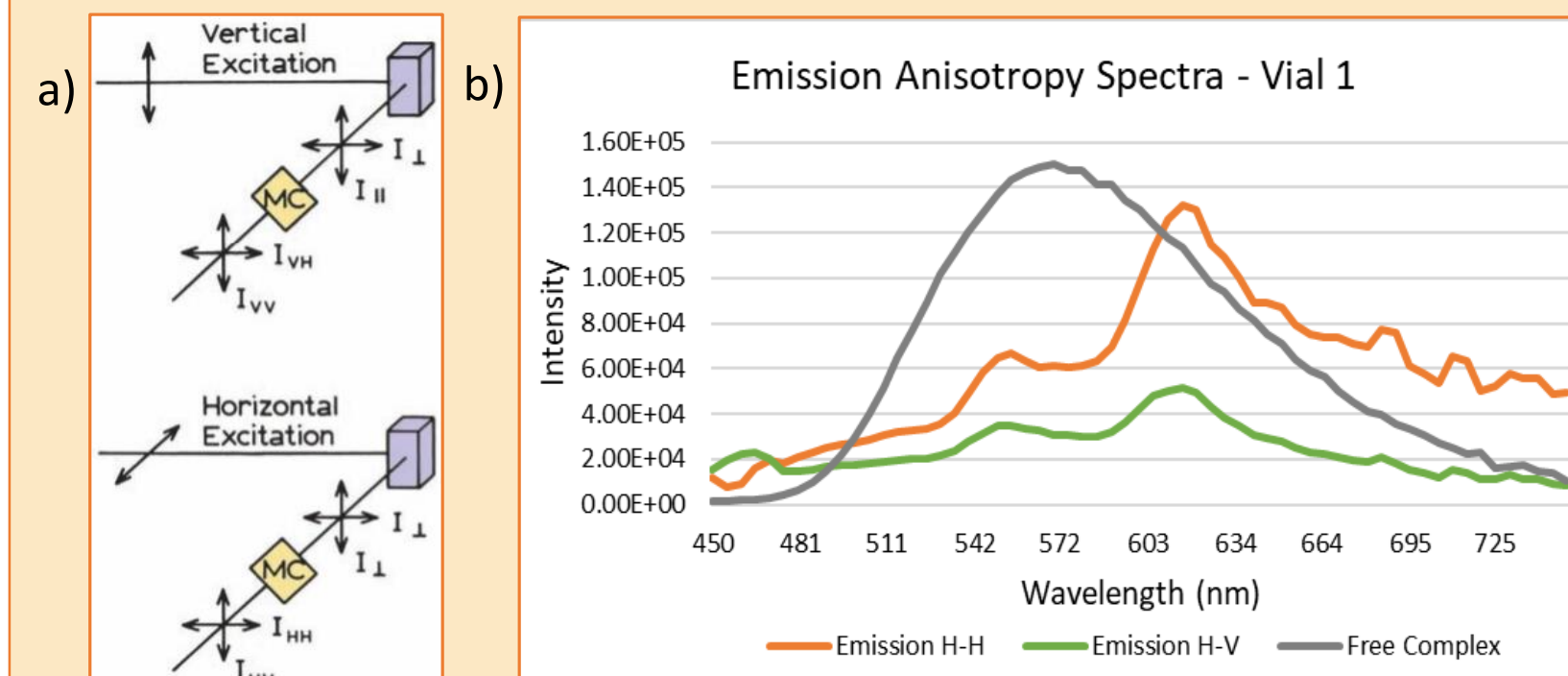


Figure 6: a) Schematic representing how anisotropy data is recorded<sup>3</sup>, b) Vial 1 data showing differences between Horizontal (H) and vertical (V) excitation/emission of the product versus the free complex in solution.

wavelength is shone onto the sample then both its intensity and any change in light orientation is detected for a range of emission wavelengths. The graph, *figure 6b*, of Vial 1's measurements corresponds to the polarisation of the excitation and the emission light, either vertically or horizontally. The large gap between the H-H (Orange) and H-V (Green) tells us that there is an imbalance in the ratio of complexes with a specific alignment of their transition dipole moments, and that light of a certain polarisation is being favoured for absorption and then emitted with a changed polarisation thus giving the large gap due to this excess of one specific orientation of crystals versus the free complexes emission curve (grey) with complexes in a random orientation.

## CONCLUSION:

To conclude this summer research, aims one and two were completed with success, with the third aim giving some undetermined results. As *figure 7* shows, there is a marked difference between the TEM (Transmission Electron Microscopy) of pure silica, and that of the synthesised product – showing a change in morphology suggesting a new compound. However, both NMR and X-Ray Crystallography were inconclusive in so far as a characterisation of the condensed zinc product, thus leaving it undetermined if the product was a successful 100% loading, or a smaller value.

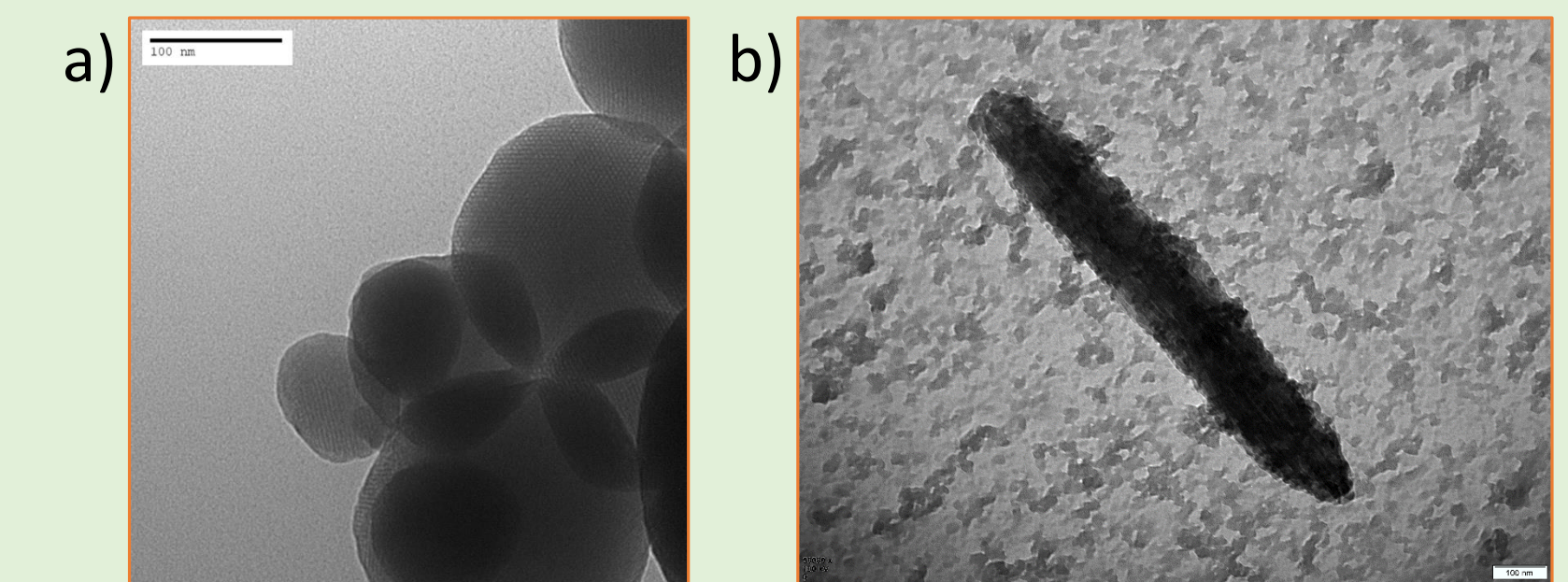


Figure 7: a) TEM image of spherical plain porous silica with ordered pores, b) TEM image of the condensed Zinc complex – Note the non-spherical crystal.

Excitation spectroscopy shown in *figure 5* confirmed that the condensed Zinc complex was indeed the same zinc complex as that of the free solution, showing very low pH levels didn't degrade the complex or hinder the condensation process. The anisotropy spectra, *figure 6b*, also shown that there is interesting internal ordering to the crystals.

## FUTURE INVESTIGATION:

- Synthesise more silylated Zinc complex to attempt to gain a clearer <sup>1</sup>H NMR spectra on the 700 MHz machine.
- Incorporate the silylated zinc powder into a conductive polymer and investigate the potential electrochemiluminescence of the compound.
- Attempt XPD (X-Ray Powder Diffraction) on the Zinc powder to uncover structure.
- Attempt elemental analysis to determine the exact Percentage (%) loading of the zinc within the polymerised complex.

## REFERENCES:

1. C. Yau, MChem thesis, Newcastle University, 2019
2. F. Zhao, D. Ma, *Mater. Chem. Front.*, 2017, 1, 1933–1950
3. J. R. Lakowicz, *Principles of Fluorescence Spectroscopy*, Springer, New York, 2006

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