Assembly Process of the Supramolecular Nanojar

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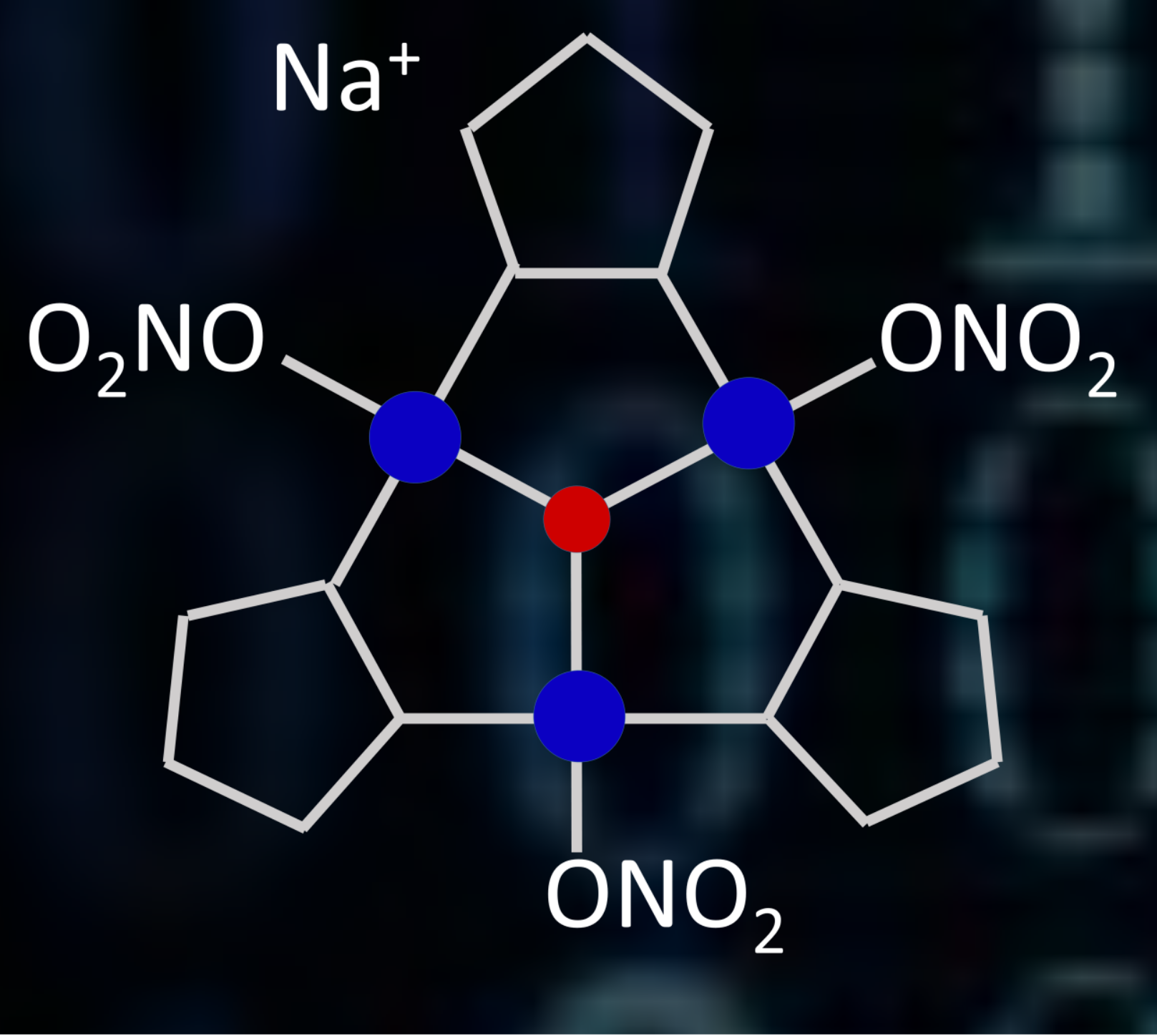
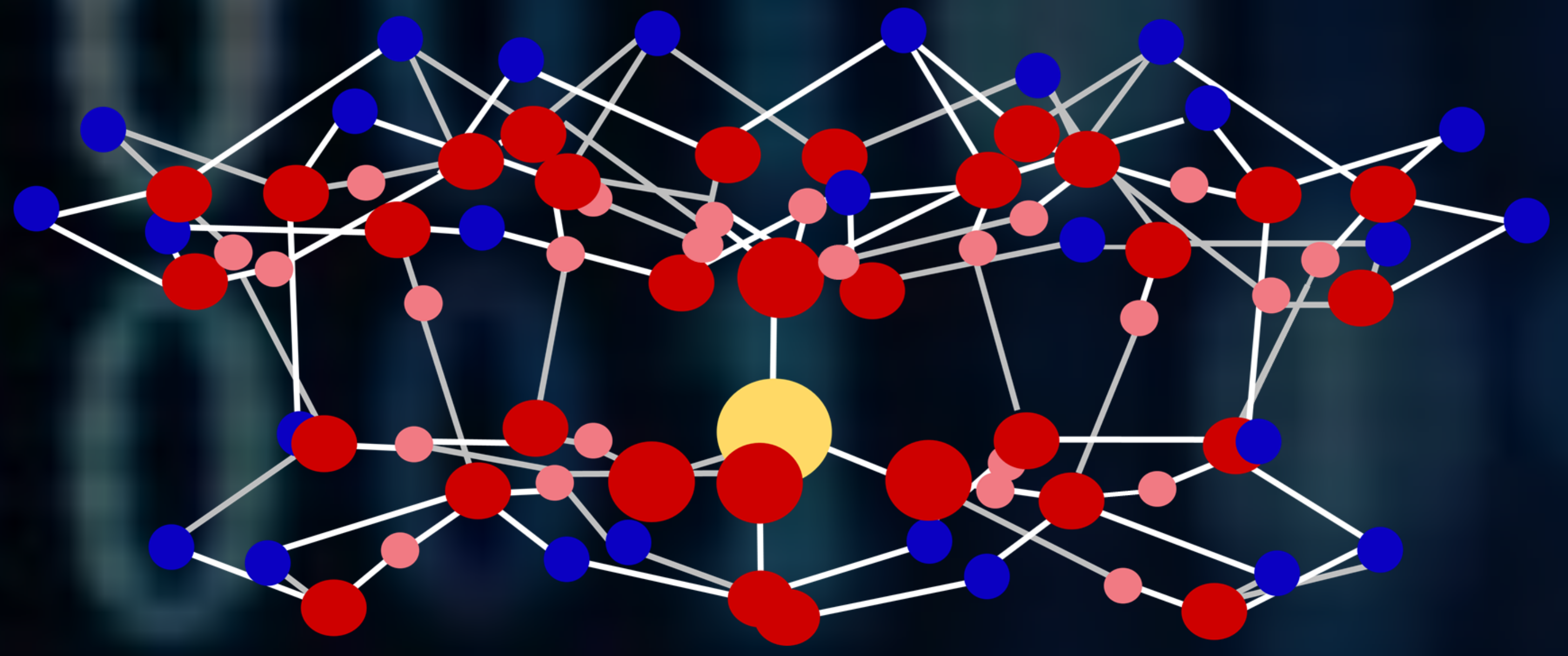
Introduction

$$31\,Cu^{2+} + 31\,Pz^{-} + 31\,OH^{-} + CO_3^{2-} \overset{?}{\rightarrow}\overset{?}{\rightarrow}\rightarrow [Cu_3Pz_3OH]^{2+} \overset{?}{\rightarrow}\overset{?}{\rightarrow}\rightarrow [CO_3^{2-} \subset (CuPzOH)_{31}]$$

Nanojars, 94-piece supramolecular structures $[CO_3^{2-} \subset (CuPzOH)_{31}]$, self-assemble around a center dianion (*Chem. Commun.*, 2012, 48, 6860–6862). These robust structures completely sequester the dianion from further reactions. We aim to learn more about the complicated assembly process of the nanojar and the intermediates that form. Mass spectrometry has shown the existence of an intermediate species known as the trimer ($[Cu_3Pz_3OH]^{2+}$) and we want to determine if there is evidence of this species in solution as well.





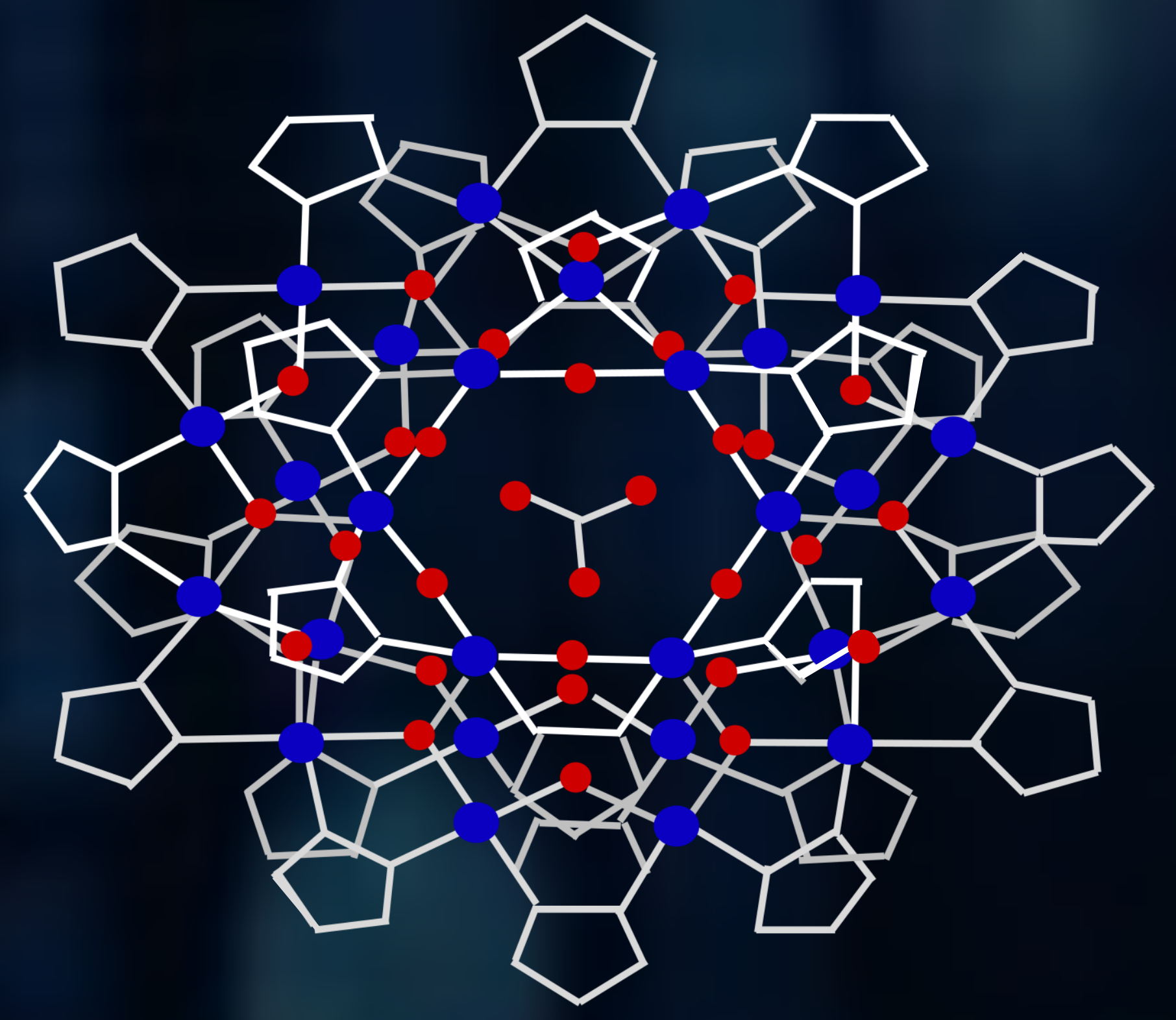
Methods

A solution's absorbance is dependent on the molar absorptivity and concentration of each species present. Spectrophotometric titrations are an effective way to study the interactions between molecules in solution because they measure the changes in absorbance as the ratio of components varies, giving insight into the reactions taking place and the species involved.

1. Performed titrations of solutions involving copper and ligand
2. Determined number of absorbing species with unrestricted factor analysis by Sivvu™
3. Tested various chemical models using equilibrium restricted factor analysis by Sivvu™
4. Calculated molar absorptivity curves and binding constants with Sivvu™

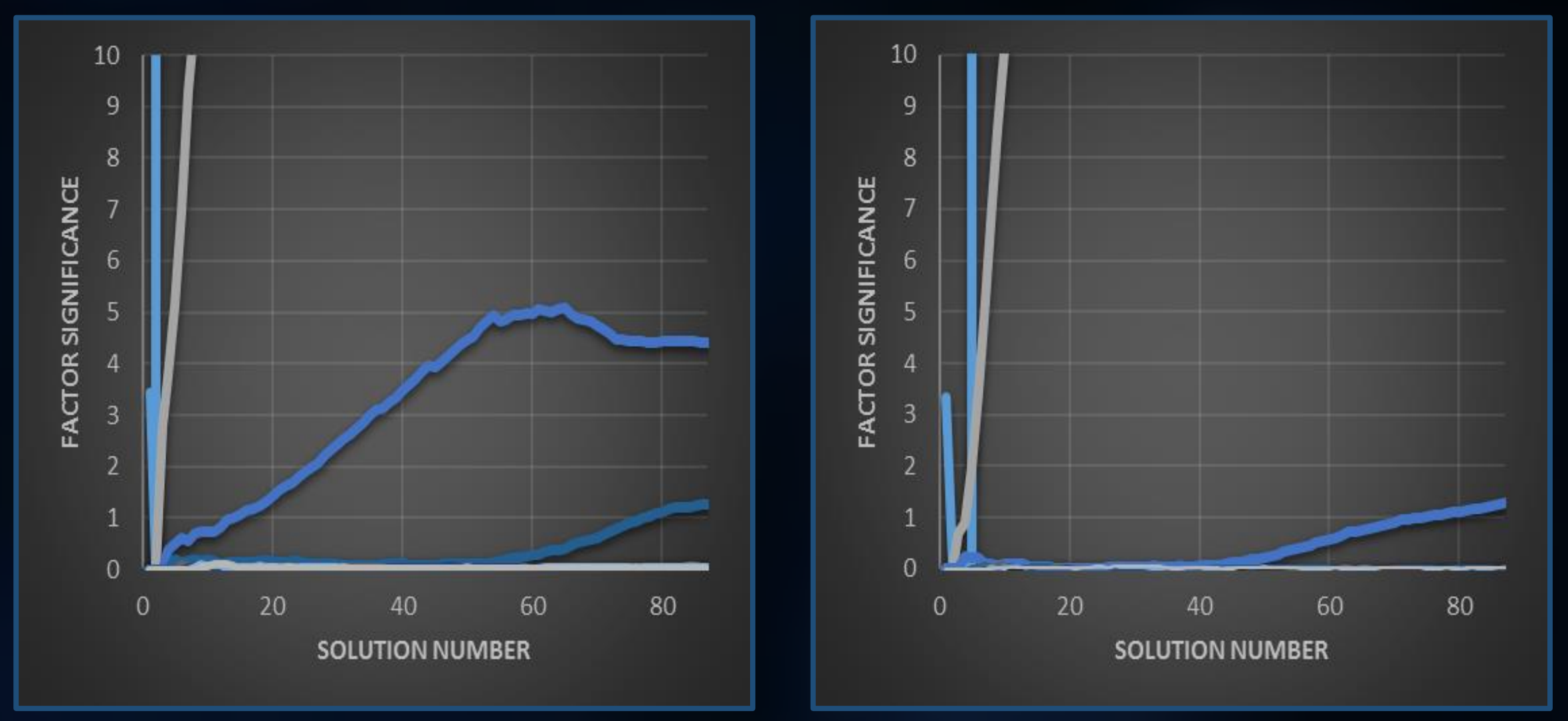
Research Questions

- Is there evidence for the existence of the trimer in solution?
- How many species are formed on the way to the trimer? What are the identities of those species?
- Is the trimer formed in both aqueous and non-aqueous titrations?



Results

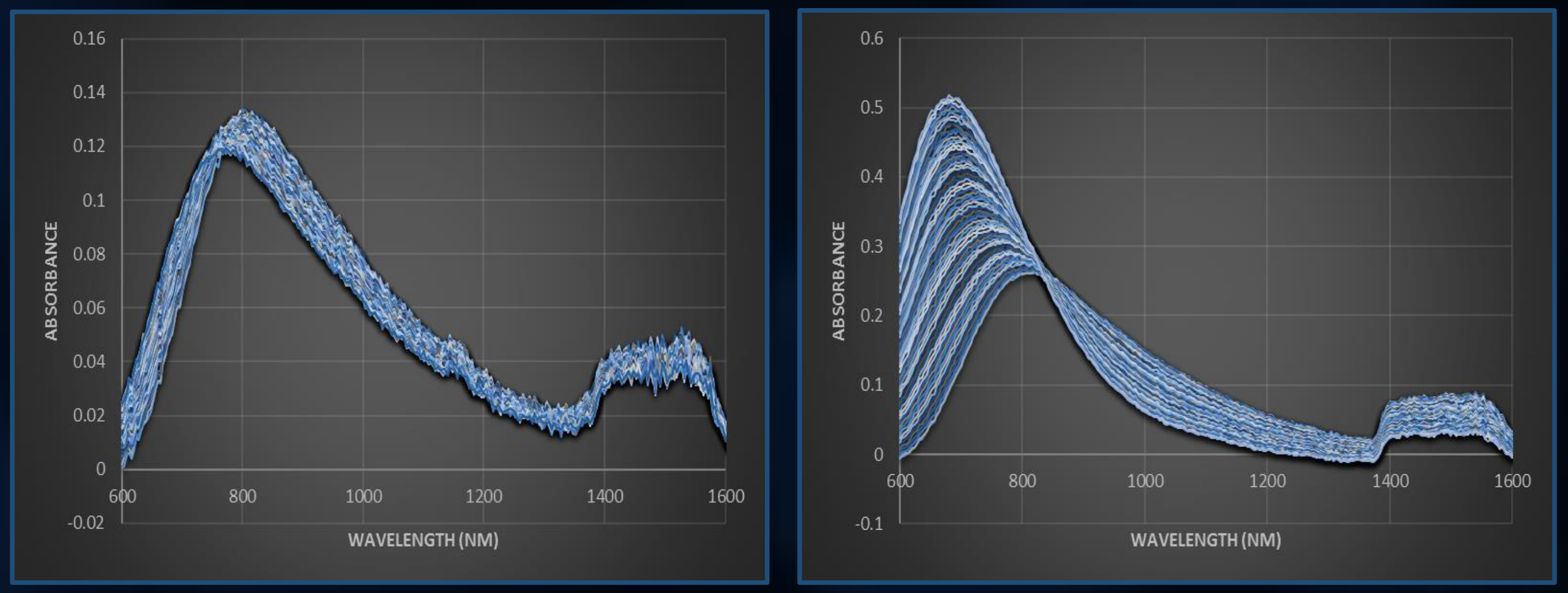
Titration of $K(CH_3)_3CO$ into 1:1 Copper/Pyrazole in Diglyme



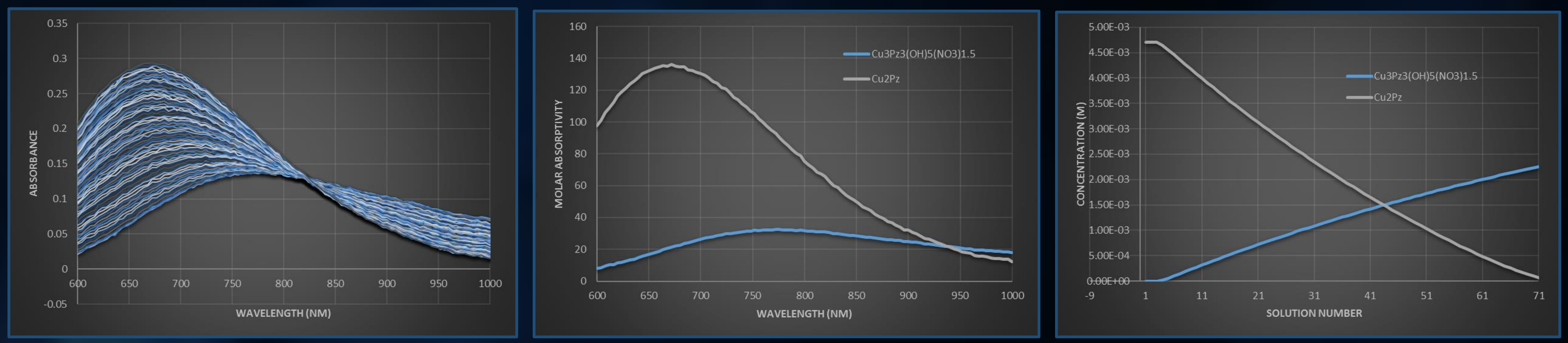
As 1.3 equivalents of t-butoxide are added, the presence of significant factors changes if additional water is present in solution. Left: 2.5 equivalents of water per Cu(II). Right: 22 equivalents.

Titration of Pyrazole into Copper up to 1:1 Ratio in Water

The presence of base changes the interactions between pyrazole and copper as it deprotonates the pyrazole. Left: No base present. Right: 1 equivalent of base in titrant solution.



Titration of NaOH into 1:1 Copper/Pyrazole in Water



Equilibrium restricted factor analysis is performed on raw absorbance data (left) from the addition of 1.3 equivalents of NaOH to calculate molar absorptivity curves (middle) and concentration profiles (right) for a Cu_2Pz, $Cu_3Pz_3(OH)_5(NO_3)_{1.5}$ model.

Conclusions

- H_2O played a key role in diglyme titrations
- No trimer found in diglyme titrations
- Trimer evidenced in H_2O titrations
- 1 or 2 additional Cu/Pz species formed
- No other Cu/Pz/OH species formed in H_2O

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