

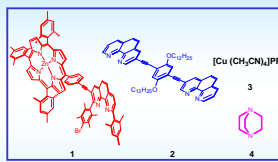
# Multicomponent Supramolecular Self-Assembly in a Single Step

Michael Schmittel, Kishore Ravuri

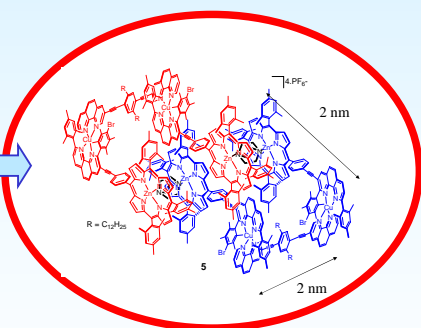
## Introduction

Nature displays a ubiquitous ability in assembling simple covalent molecules into tertiary supramolecular aggregates utilising diverse binding modes (hydrogen bonding, metal co-ordination,  $\pi$ - $\pi$  interactions, salt bridges). An ideal mimic of natural self-assembly would involve a number of simple molecular components, each contributing specific molecular information as an input which, under equilibrium conditions would evolve one preferred, most stable multicomponent self-assembly. Although a number of examples are known,<sup>1</sup> designing and accessing a multicomponent self-assembly still remains a difficult task. Herein we demonstrate a simple approach to one such assembly **5** via a single reaction step utilising orthogonal and non-interfering binding algorithms. As a tool-kit we have used Cu<sup>+</sup> directed heteroleptic bisphenanthroline complexation (HETPHEN)<sup>2</sup> and the zinc porphyrin-DABCO binding motif.<sup>3</sup>

### Constituent molecular components

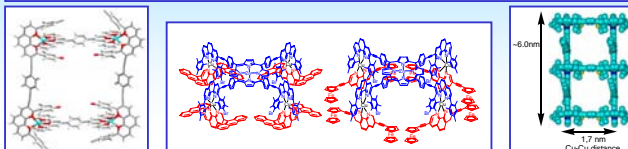


2 : 1 : 1 (or 1.5) based on the principle of maximum site occupancy.

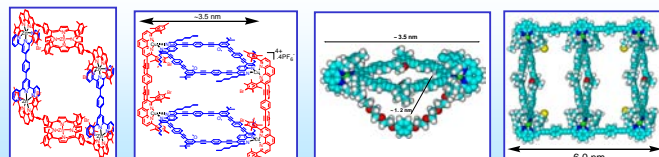


### HETPHEN approach as a tool for supramolecular self assembly

We have previously used the HETeroleptic bisPHENanthroline complexation approach to access a variety of supramolecules in the nanometer regime.

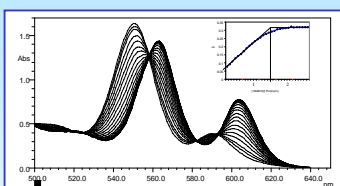


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Helmut Cölfen, Jan W. Bats, *J. Am. Chem. Soc. In Press*  
M. Schmittel, V. Kalsani, D. Fenske, A. Wiegrefe, *Chem. Commun.* **2004**, 490-491.

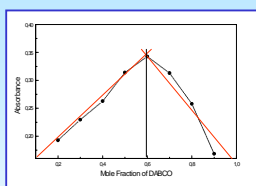


M. Schmittel, H. Ammon, V. Kalsani, A. Wiegrefe, C. Michel, *Chem. Commun.* **2002**, 2566-2567.  
V. Kalsani, H. Ammon, F. Jäckel, J. P. Rabe, M. Schmittel, *Chem. Eur. J.* **2004**, *10*, 5481-5492.

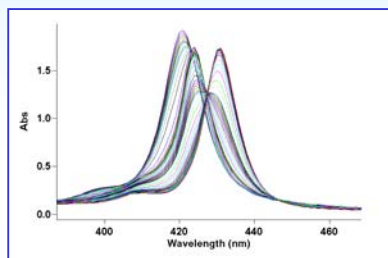
## UV investigations



UV titration of **6** against DABCO at  $\mu$ M concentration.



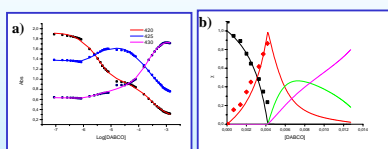
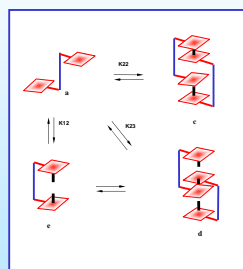
Jobs plot analysis showing a 1:1.5 composition of **6** vs DABCO.



Constant	log $\beta$
K22	15.6 $\pm$ 0.8
K23	21.3 $\pm$ 0.4
K12	9.7 $\pm$ 0.2

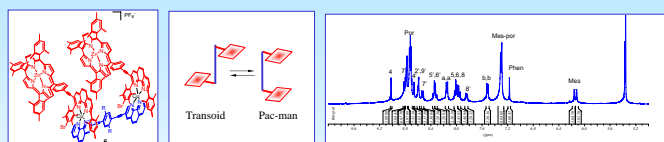
Binding constants were calculated using SPECFTT

Binding constants were calculated from titration data obtained from the Soret band shifts. The data fitted well to a four state binding model which could be explained through a model below.

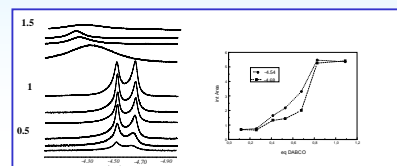


a) The experimental data fitted well to a four state binding model, (the solid lines represents simulated data and the dots represent the experimental data).  
b) Fitting of the NMR titration data to the four state binding model obtained from the UV titration data

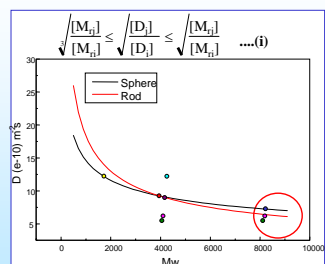
## NMR investigations



Supramolecular complex **6** was prepared and titrated against DABCO in order to investigate the nature of the assembly **5**.



<sup>1</sup>H NMR titration revealed that two signals shifted upfield at -4.54 and -4.68 ppm. The development of the NMR signals levels off by addition of 1.5 eq of DABCO providing an assignable set of signals.



Complex	Diffusion coefficient (e <sup>-10</sup> m <sup>2</sup> /s)
1-Cu-Phenanthroline	12.2
5	9.2
5+DABCO 1:1	5.5
5+DABCO 1:1.5	7.3
5+DABCO excess	8.9
5+Bipyridyl 1:1	6.2
5+Bipyridyl excess	12.2

Further proof for the formation of the multicomponent supramolecular assembly came from diffusion coefficient obtained from DOSY experiments on NMR. The calibration curve was obtained using equation (i) which is an inverse relationship between the molecular weight and diffusion coefficient. It was clear from the curve that the diffusion coefficient of **5** corresponded to a molecular weight  $\approx$  8000 corresponding to the composition predicted

## Conclusions

Based on the principles of non interfering and orthogonal binding algorithms and maximum site occupancy, we have obtained a multicomponent self assembly which exhibits unique binding behaviour with DABCO.

## Acknowledgements

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