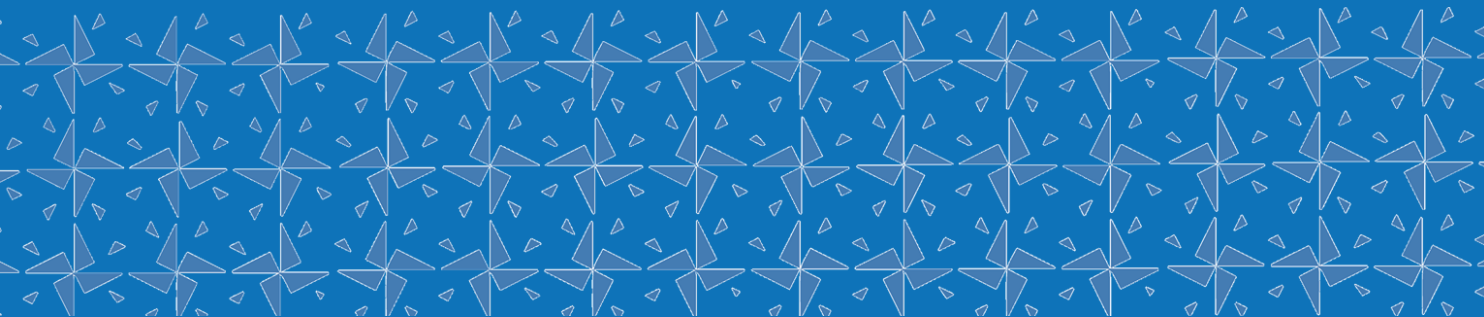




Trinity College Dublin

Coláiste na Tríonóide, Baile Átha Cliath

The University of Dublin



Core Modulation of Porphyrins for Chemical Sensing

Karolis Norvaiša

Under supervision of Prof. Dr. Mathias O. Senge



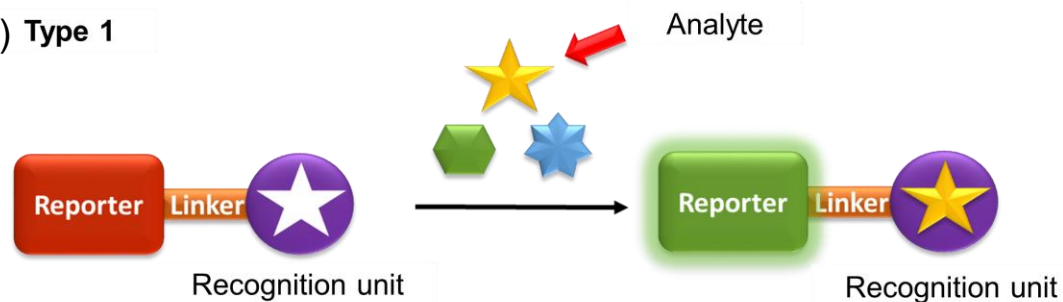
**Senge
Group**



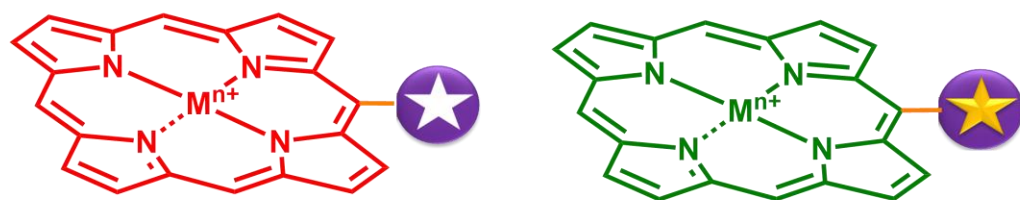
Two Most Common Sensing Platforms

- a) Separate recognition and reporter units are linked together;
- b) Receptor and reporter functions as one organic framework.

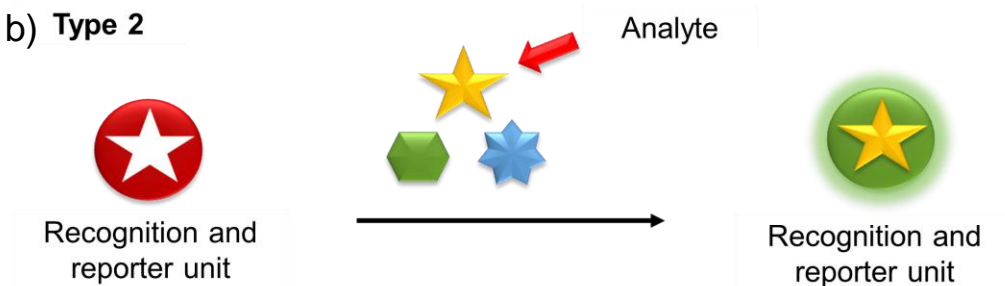
a) Type 1



e.g.



b) Type 2



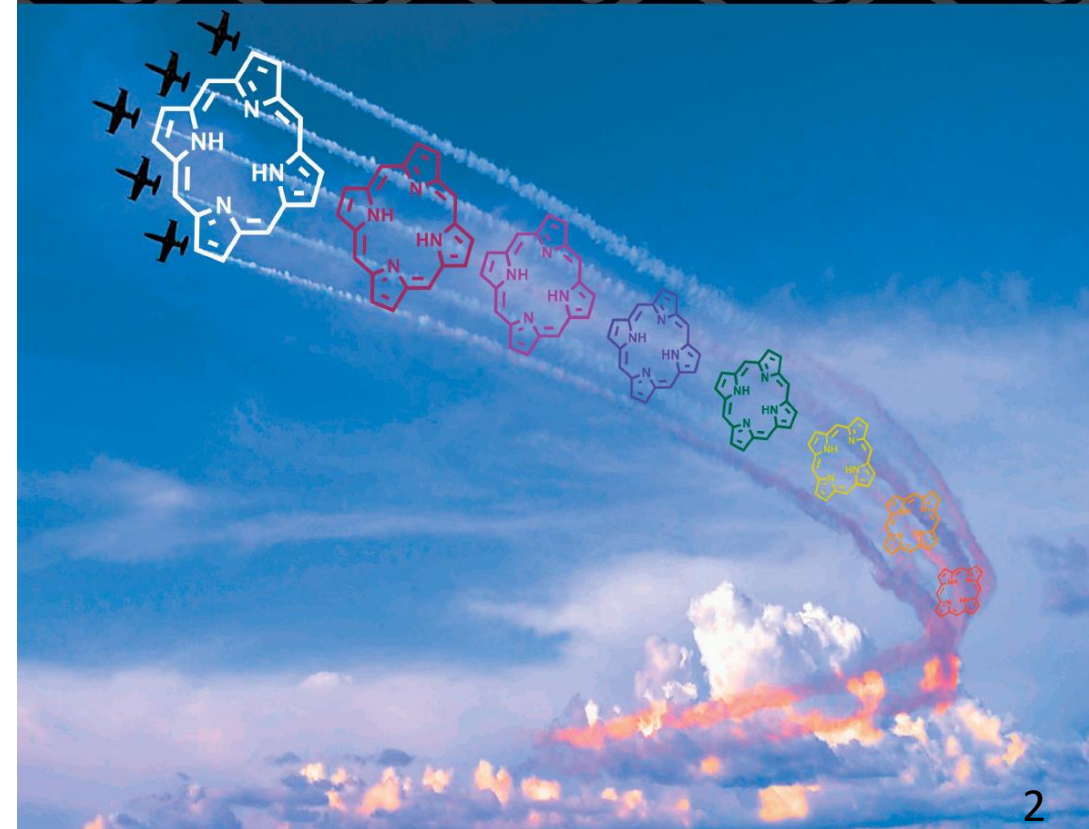
e.g.



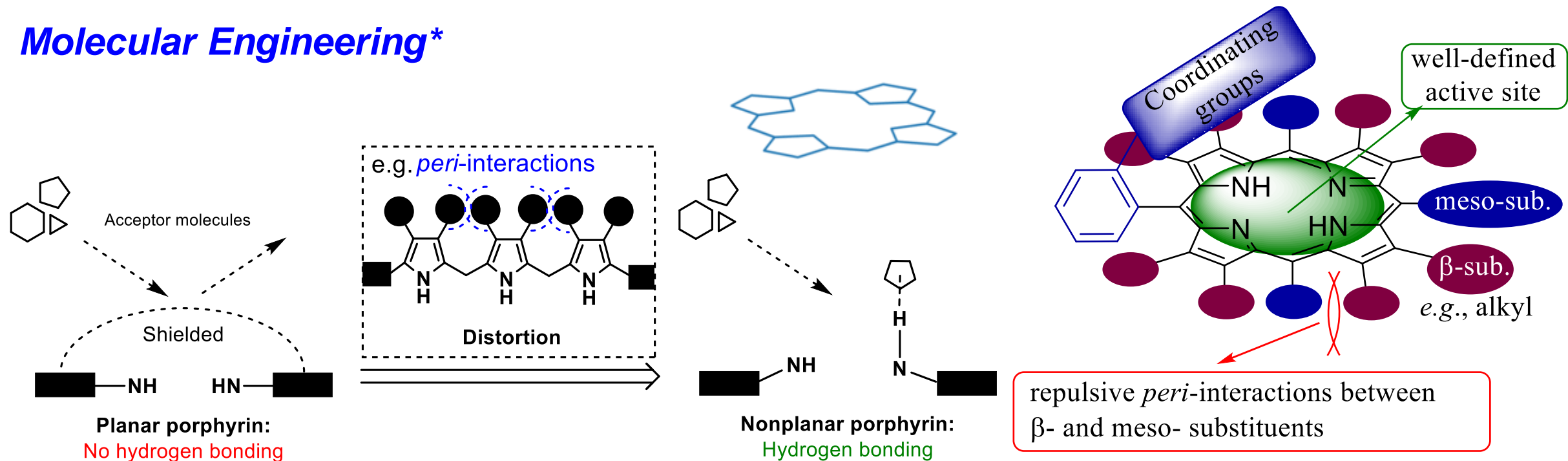
Front Cover:

M. O. Senge et al.

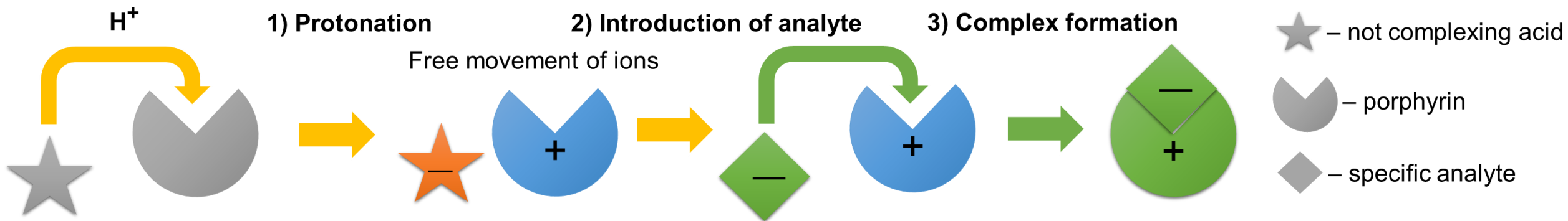
Porphyrins as Colorimetric and Photometric Biosensors in Modern Bioanalytical Systems



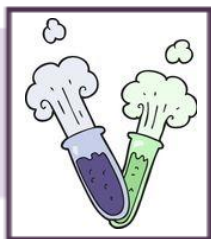
Molecular Engineering*



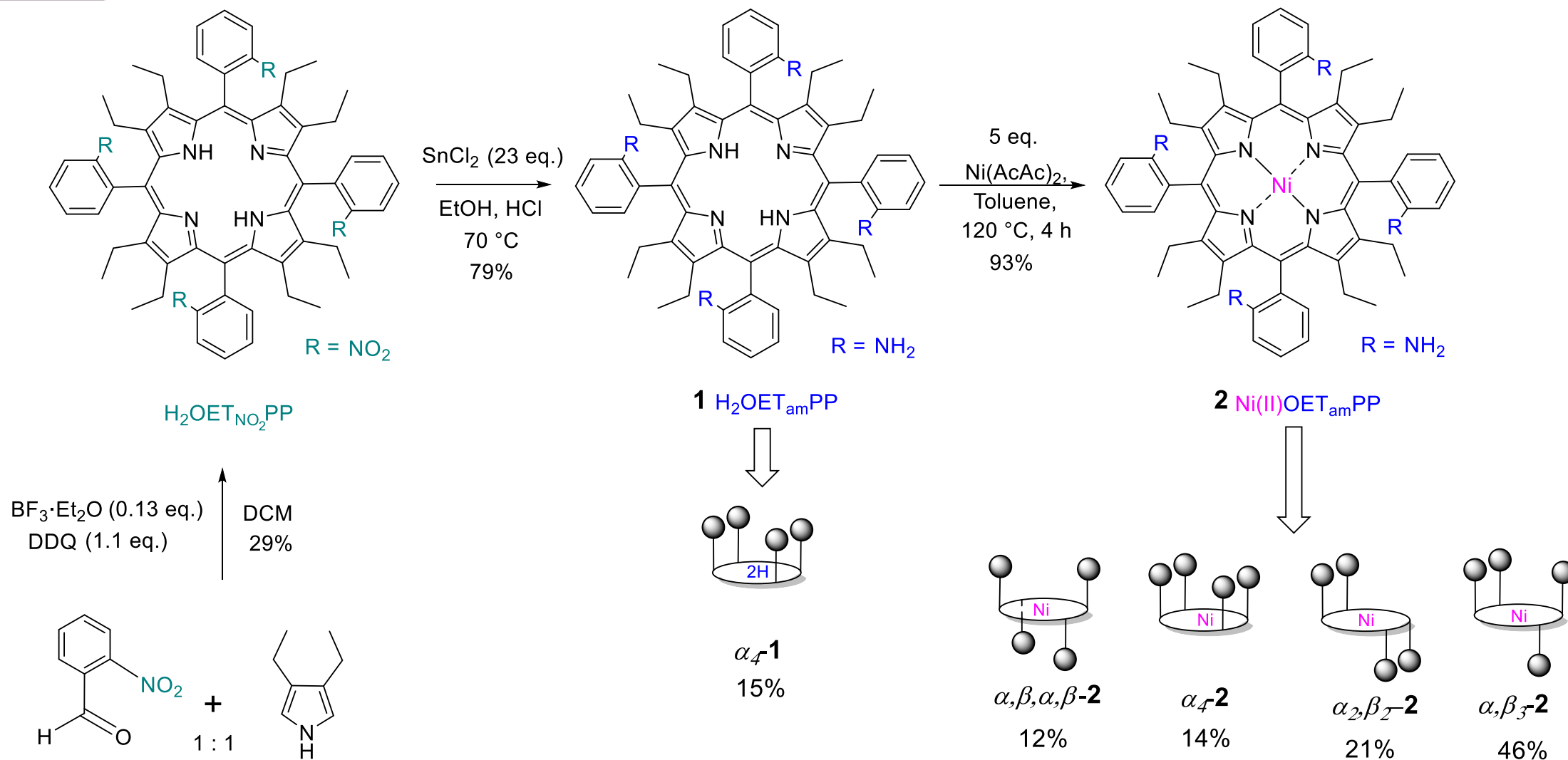
Strategy



*M. Kielmann and M. O. Senge, *Angew. Chem. Int. Ed.*, **2019**, 58, 418–441.

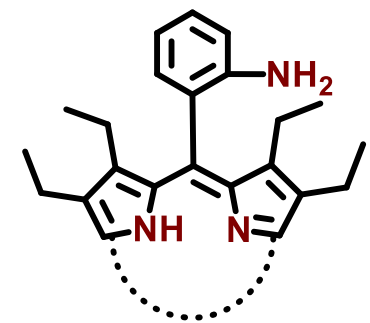


Synthesis

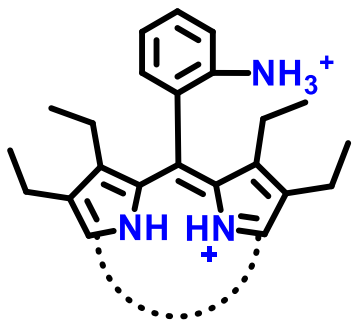


UV-vis Responses of the Porphyrin Receptor to Analytes

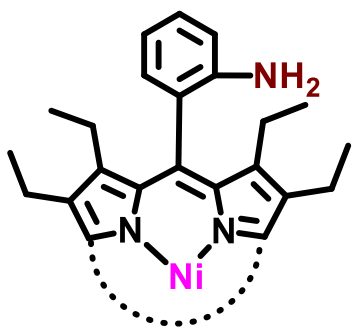
Studies carried out in chloroform



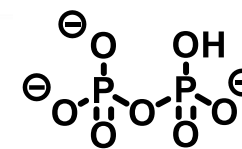
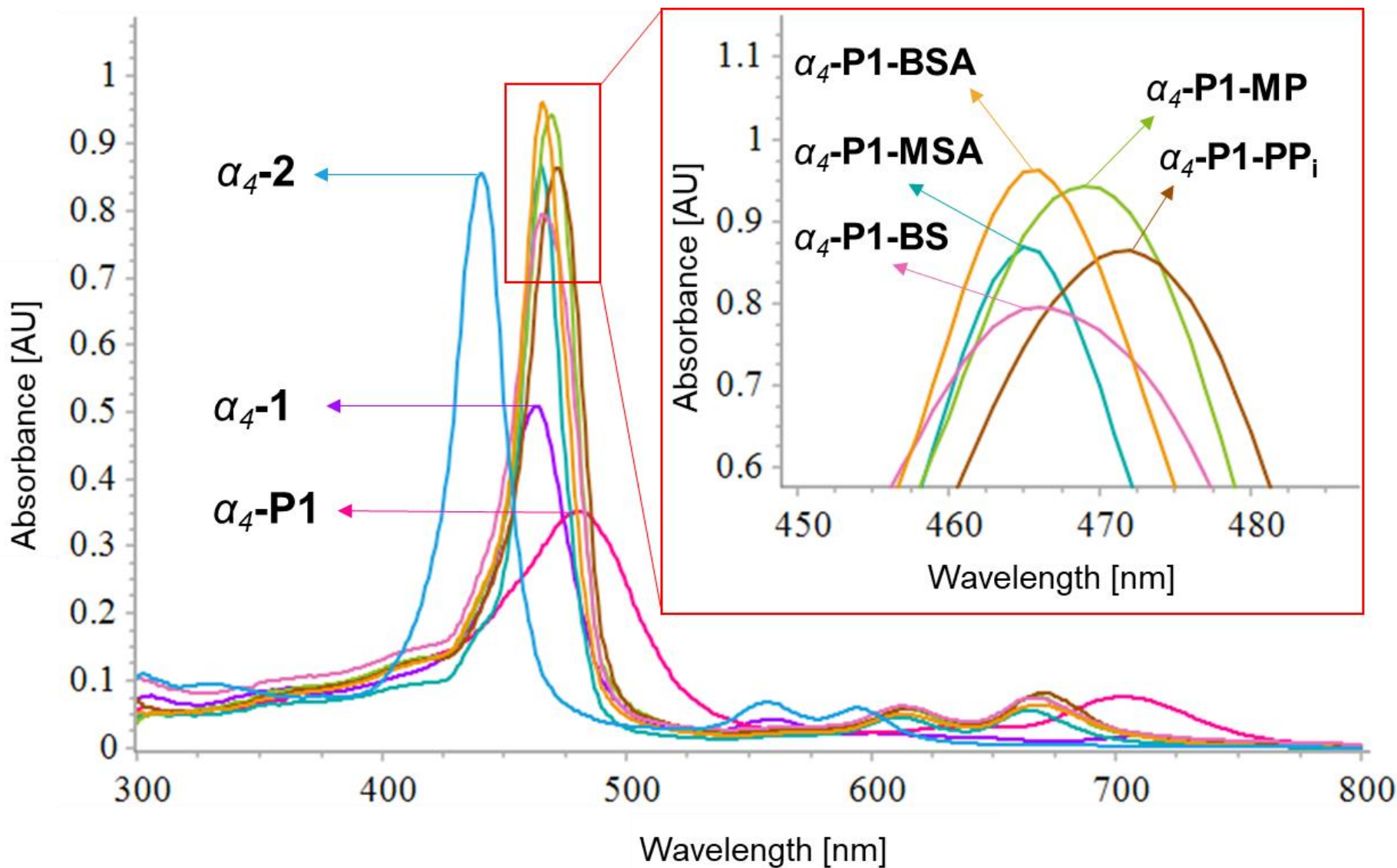
a_4-1 $H_2OETP_{am}P$



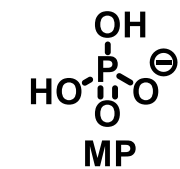
a_4-P1 $H_6OETP_{am}P^{6+}$



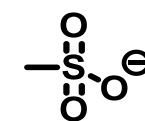
a_4-2 $NiOETP_{am}P$



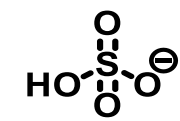
PP_i



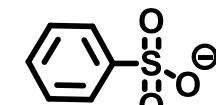
MP



MSA



BS



BSA



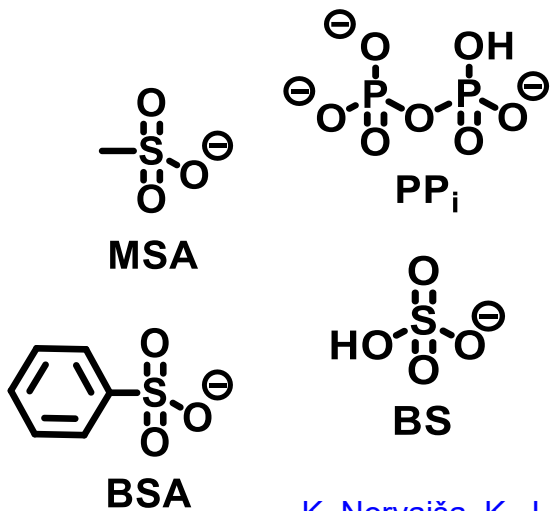
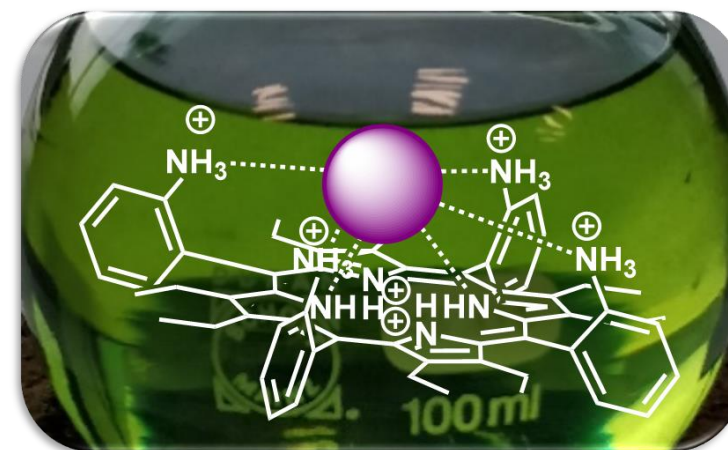
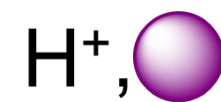
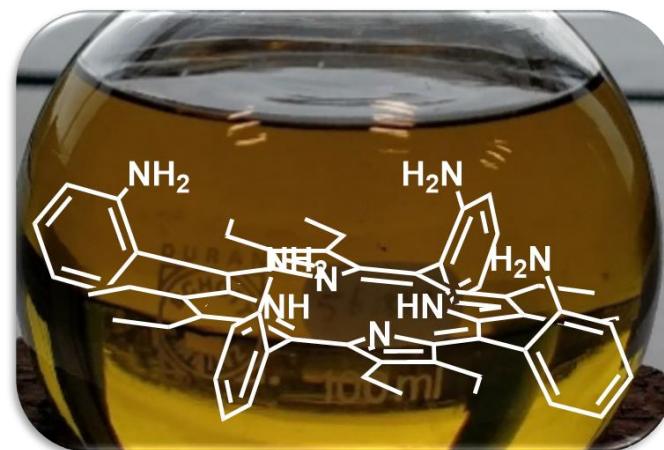
Switchable, Colorimetric Binding Modes

Colorimetric responses performed in acetonitrile

COLORIMETRY AND REVERSIBILITY

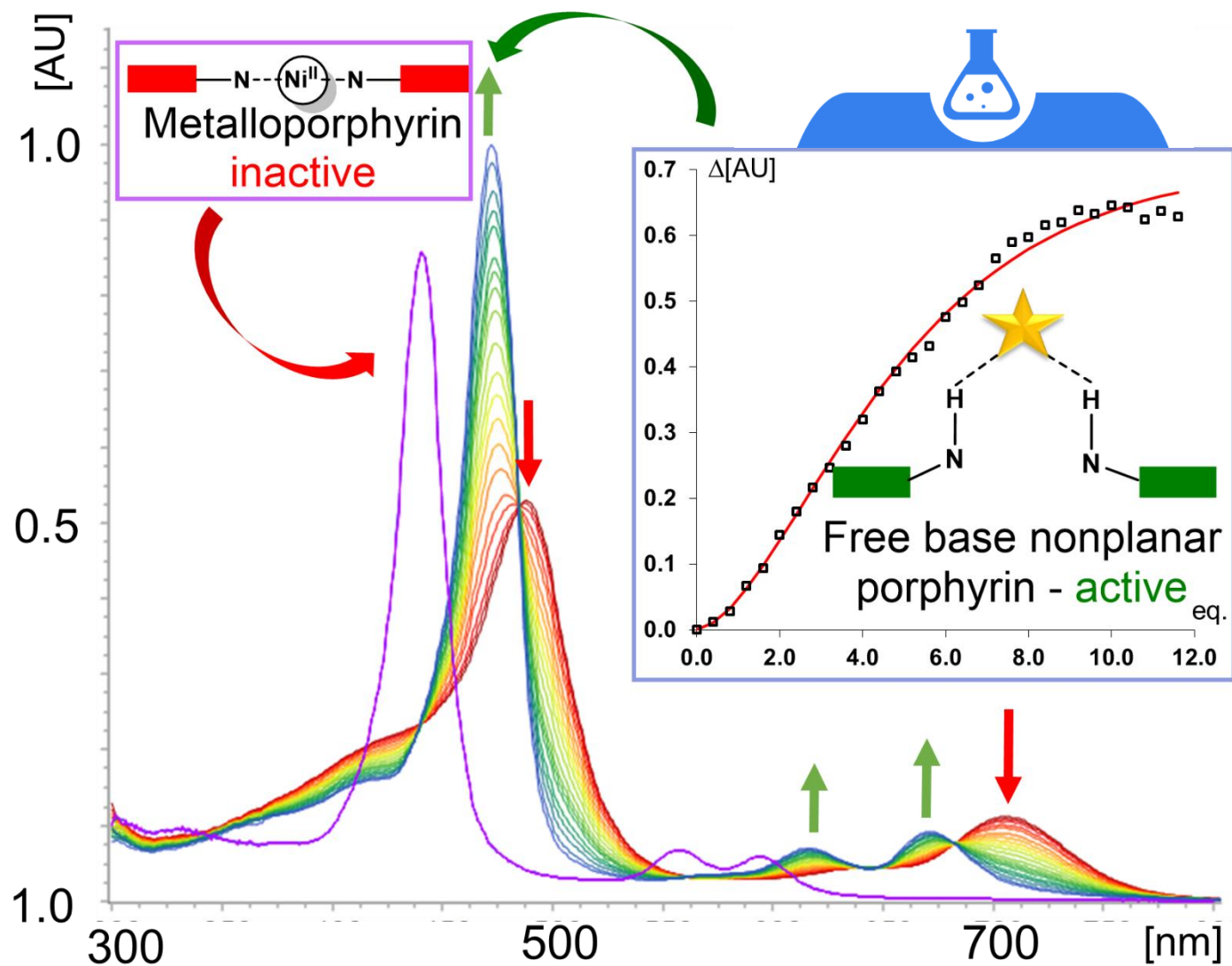
Colorimetric transition from yellow/brown to green upon substrate coordination

Binds analytes in a switchable manner dependent on the acidity of the solution



Confirmation of N-H...X-type Binding Mode

Studies carried out in chloroform



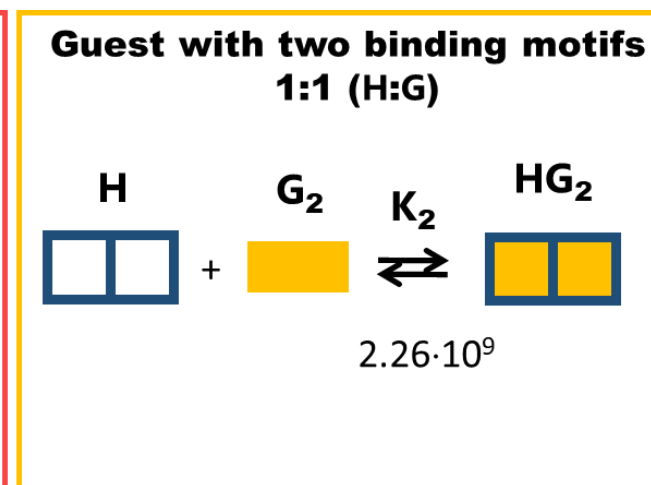
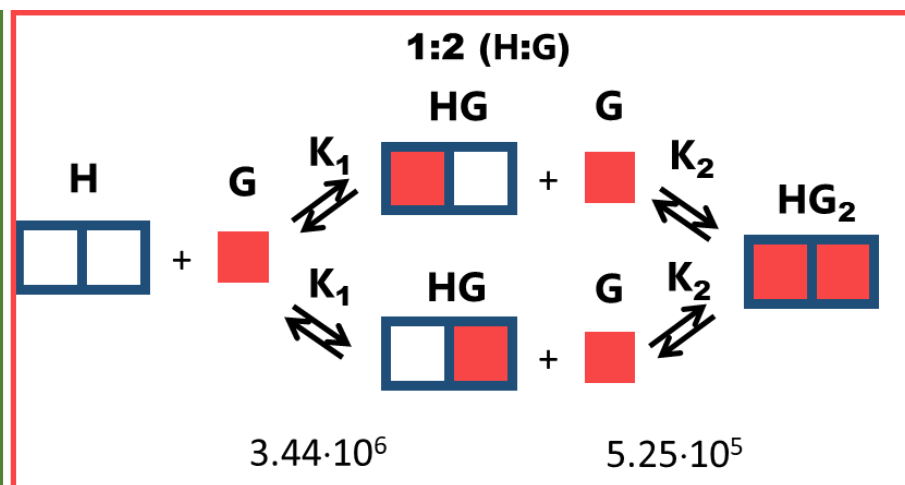
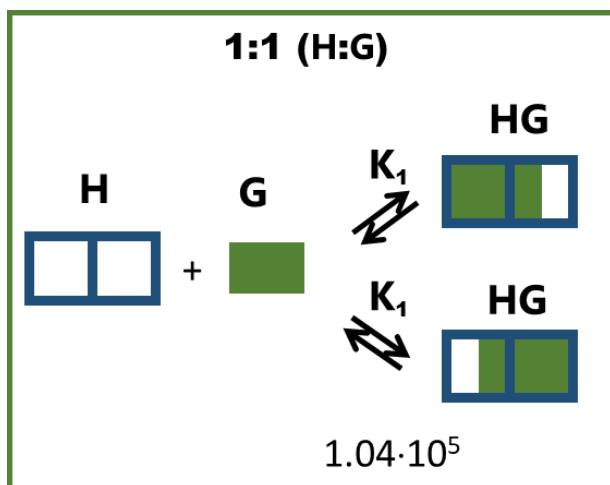
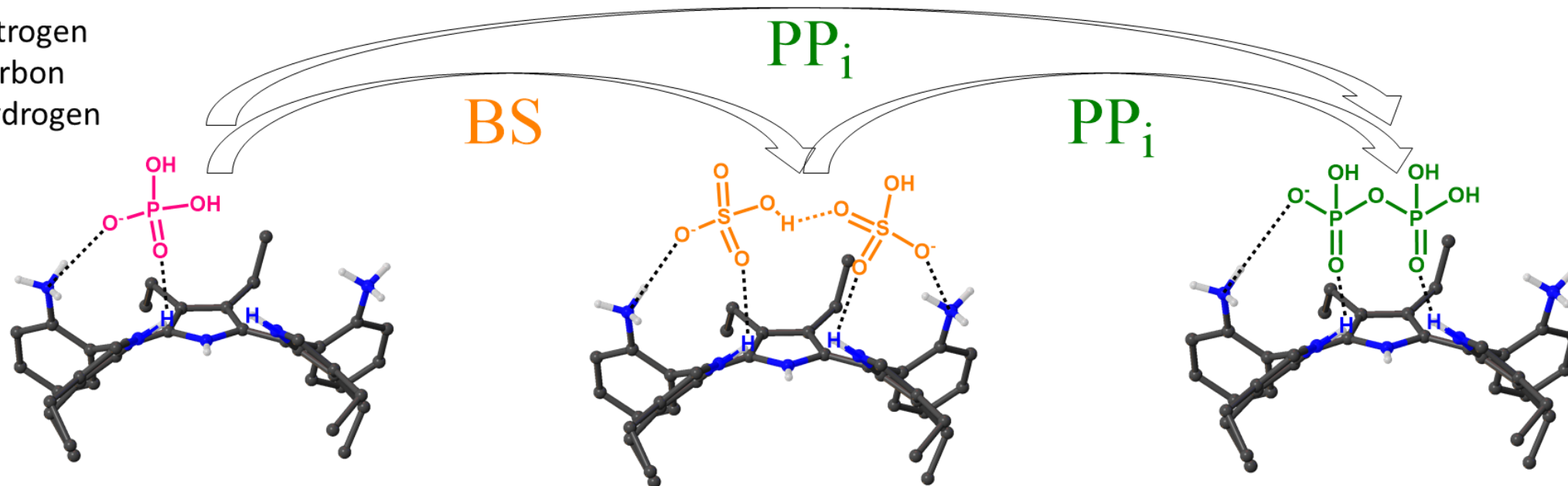
A porphyrin-based sensor . . .

... for selective detection of anions is described by M. O. Senge and co-workers in their Communication on page 16553. The acid-activated interface between the specially designed binding cavity and corresponding substrates results in distinct spectroscopic alterations with a vibrant colorimetric response. The cover picture by Ella Marushchenko illustrates chemically re-engineered pigments behaving like tiny Venus flytraps that lure anions depicted as flies.

Binding and Displacement Studies

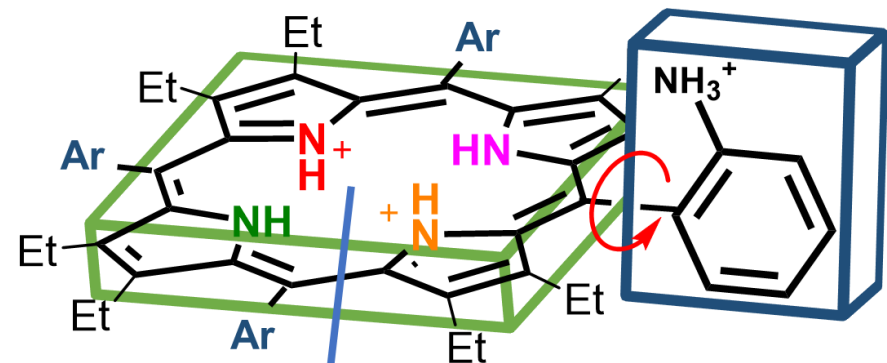
Studies carried out in chloroform

- – Nitrogen
- – Carbon
- – Hydrogen

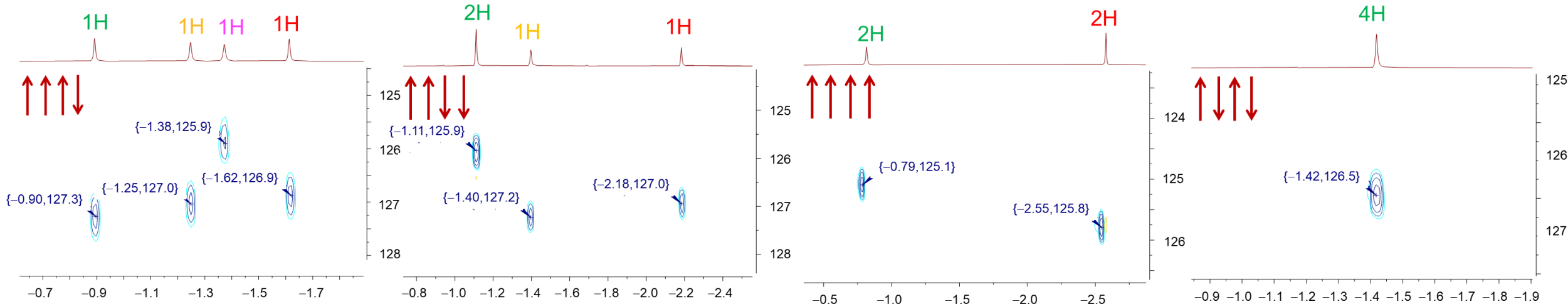


Identifying Atropisomerism by NMR Studies

Studies carried out in d_3 -acetonitrile and BSA

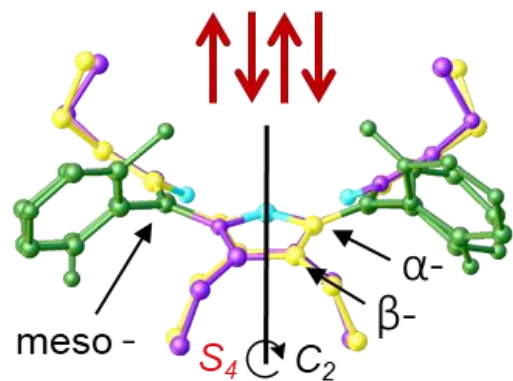
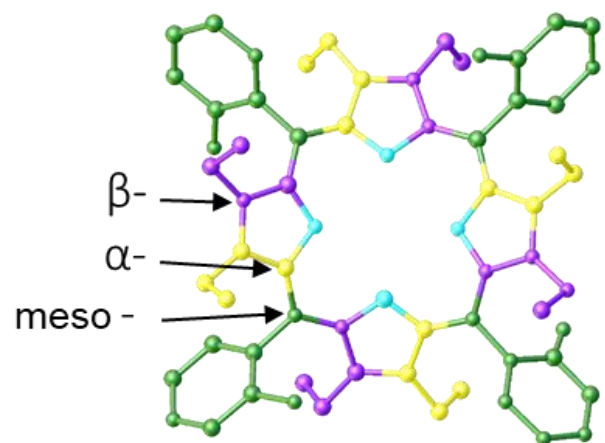


$^1H-^{15}N$ HSQC



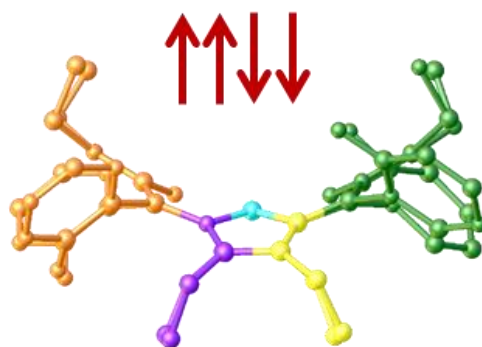
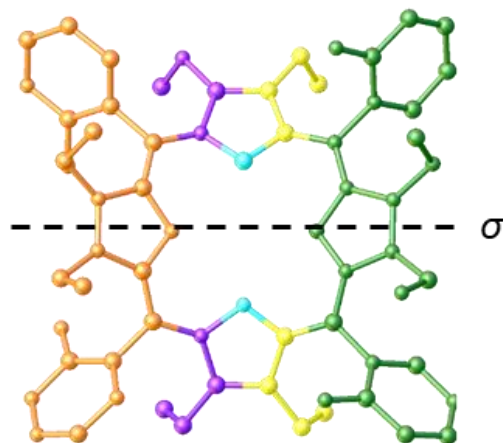


Symmetry Determination in All Atropisomers



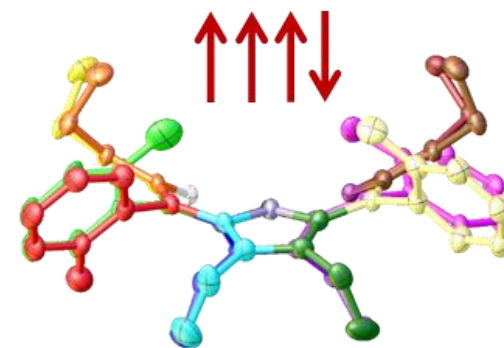
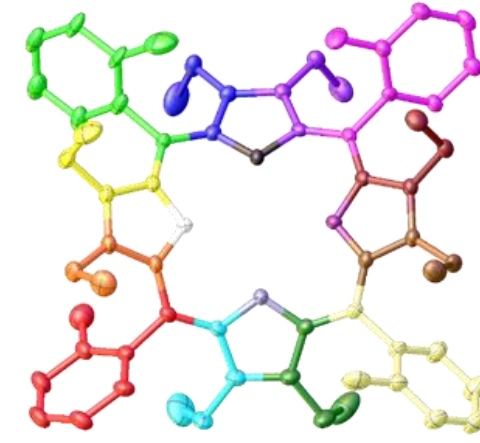
Point group {order} S_4 {4}

Planar* D_{2d} {8}



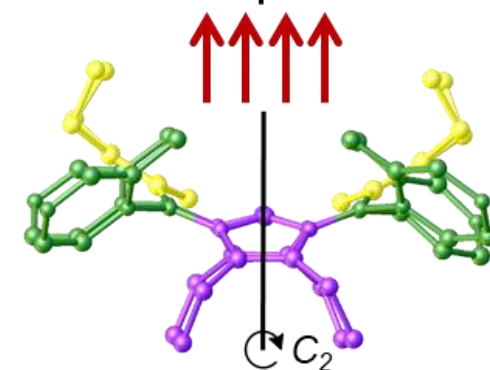
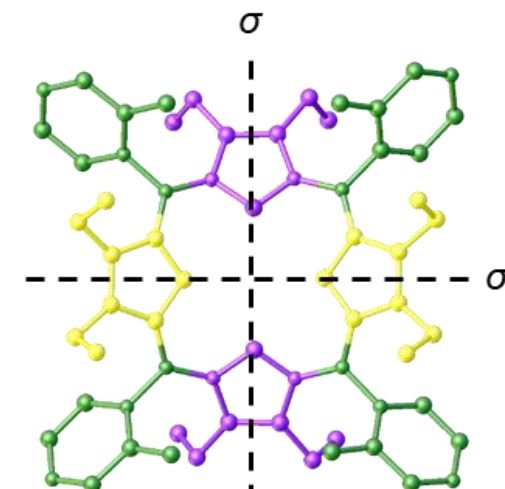
C_s {2}

C_{2h} {4}



C_1 {1}

C_s {2}



C_{2v} {4}

C_{4v} {8}

Acknowledgements

Under the supervision of Prof. Dr. Mathias O. Senge

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**Thank you for
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Zoi Melissari
Claire Donohoe
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