The 1st International electronic Conference on Chemical Sensors and analytical Chemistry (CSAS 2021)

Theoretical rationalization of chirality sensors on the basis of mono- and bis-porphyrins

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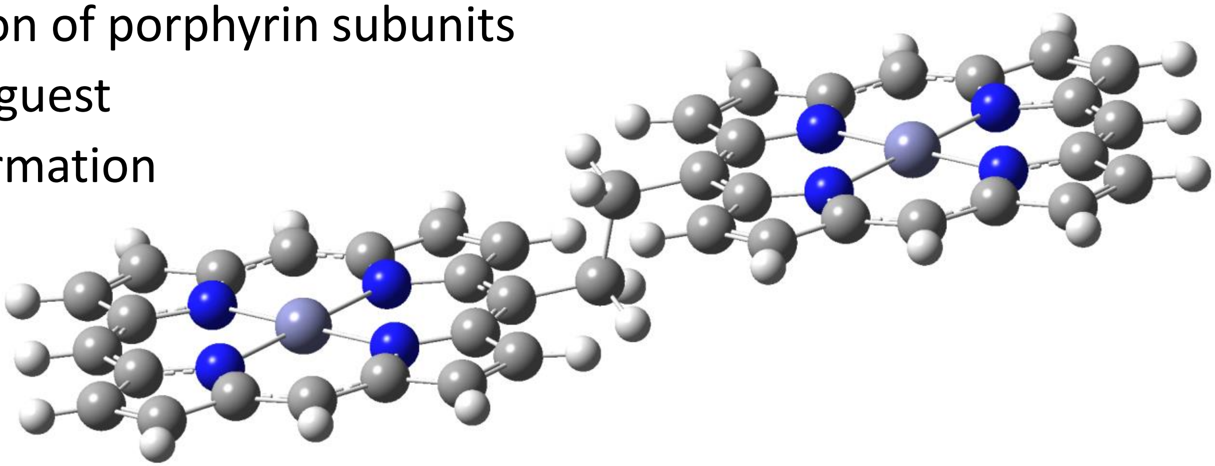
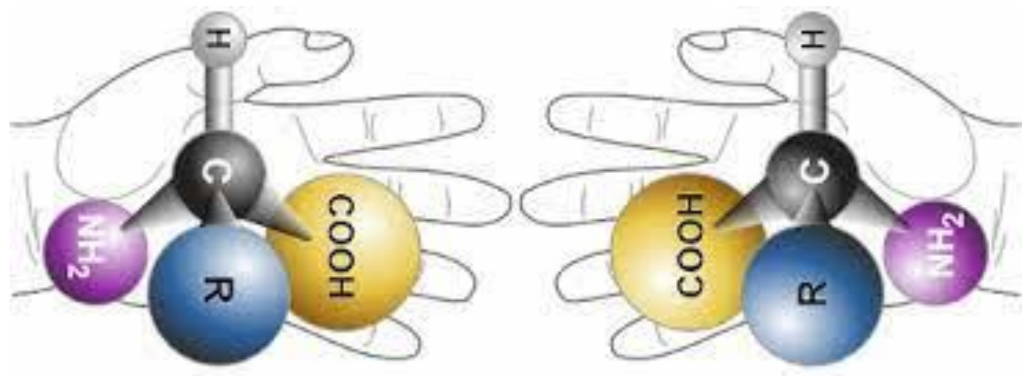
Content

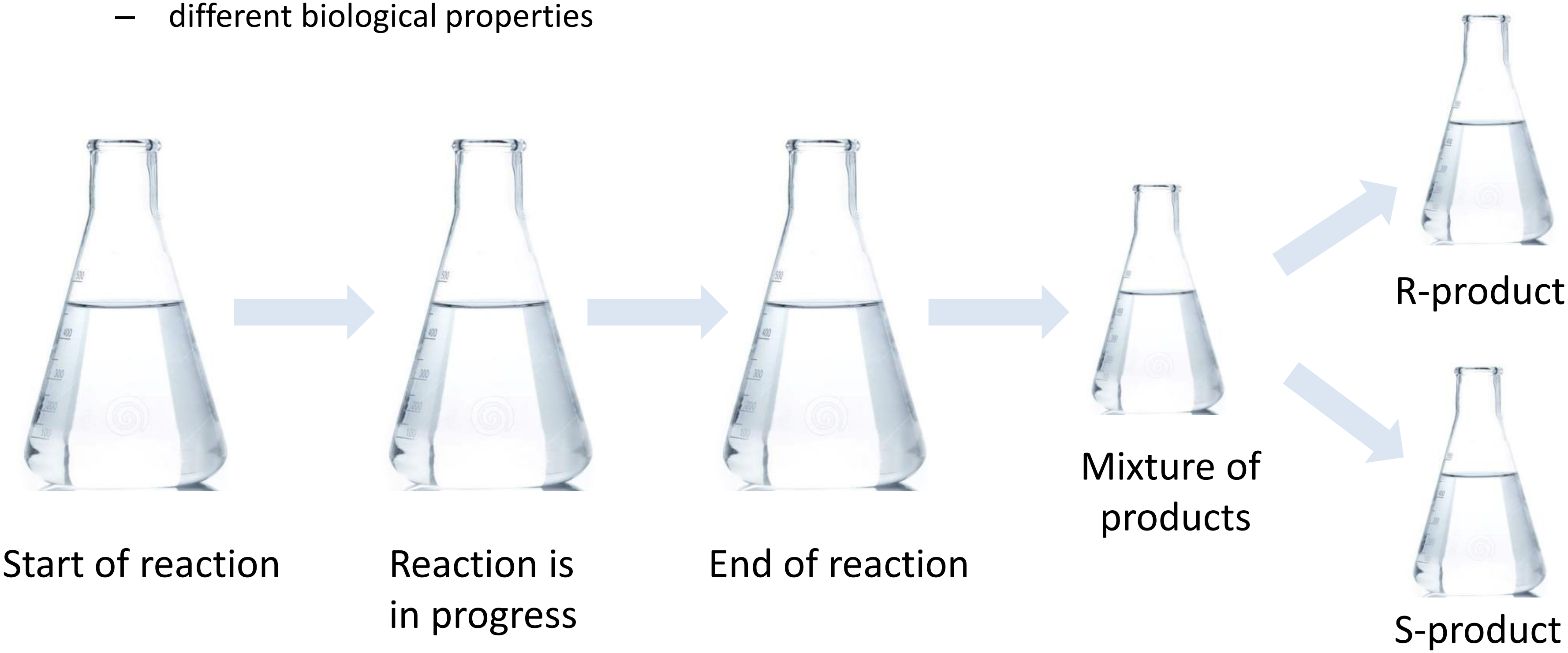
- Introduction
  - Chirality
  - Circular dichroism
  - Porphyrins
- Sensors based on monoporphyrins
  - Influence of other chromophores
    - guest
    - peripheral substituents
  - Influence of porphyrin plane distortion
- Sensors based on bisporphyrins
  - Influence of position of porphyrin subunits
  - Influence of chiral guest
  - Influence of conformation



Chirality

- Enantiomers:
  - One stereocenter
  - same physical properties
  - different biological
- Diastereomers:
  - Several stereocenters
  - different physical properties
  - different biological properties

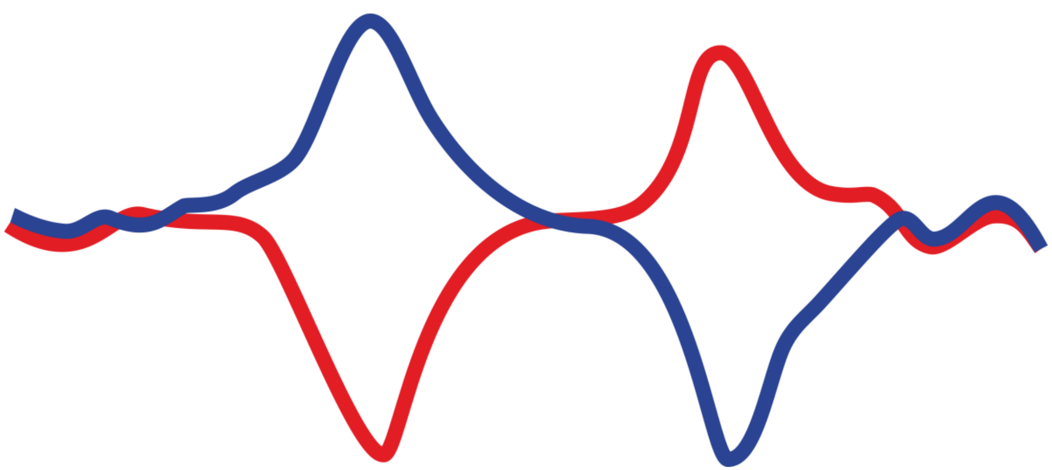




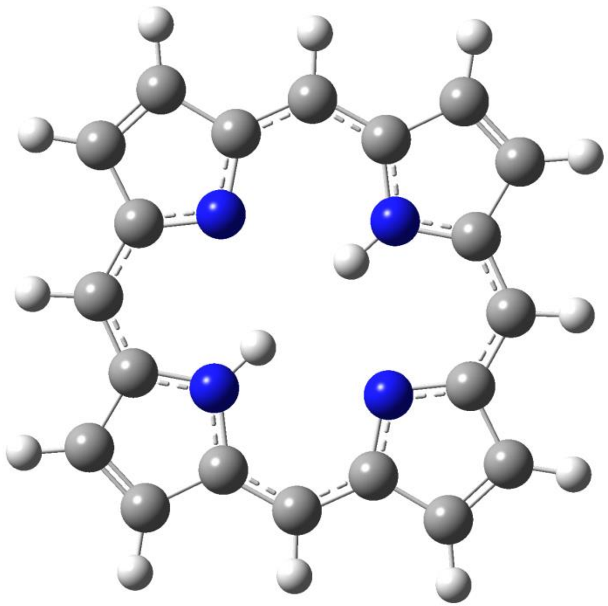
Circular dichroism

- Circular dichroism (CD) is an absorption spectroscopy method based on the differential absorption of left and right circularly polarized light.
- For non silent CD spectra, investigated molecules should be chiral and have both electric and magnetic transition moments.

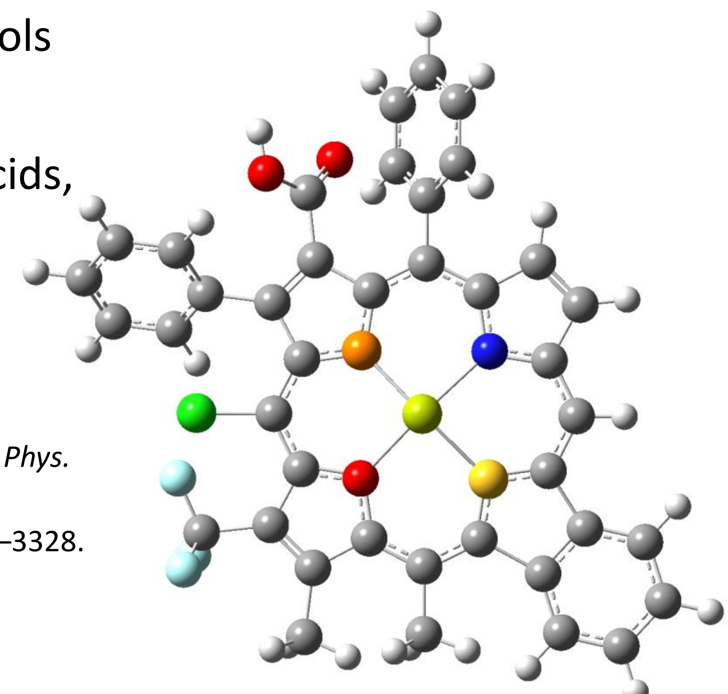
$$R = Im(\mu \cdot m)$$



Porphyrins



- Unique physical properties
- Electric and magnetic transition moments
- Ability to bind vide range of organic compounds:
  - diamines,
  - amino acid derivatives,
  - amino alcohols
  - alcohols,
  - carboxylic acids,
  - epoxides….



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- Ishihara, S.; Labuta, J.; Van Rossom, W.; Ishikawa, D.; Minami, k.; Hillab J. P.; Ariga K.; *Phys. Chem. Chem. Phys.*, **2014**, *16*, 9713-9746.
- Chatterjee, T.; Shetti, V.S.; Sharma, R.; Ravikanth, M.; *Chem. Rev*. **2017**, *117*, 4, 3254–3328.
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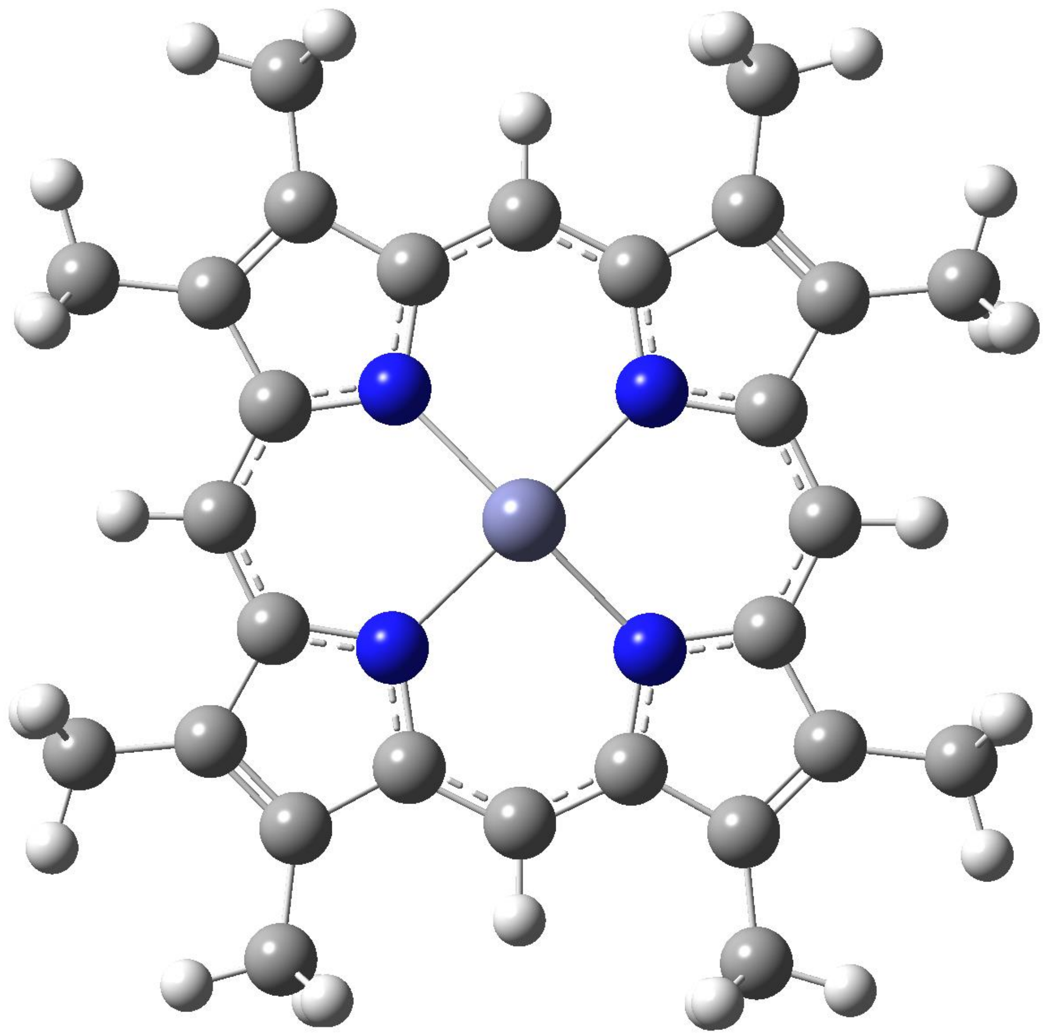
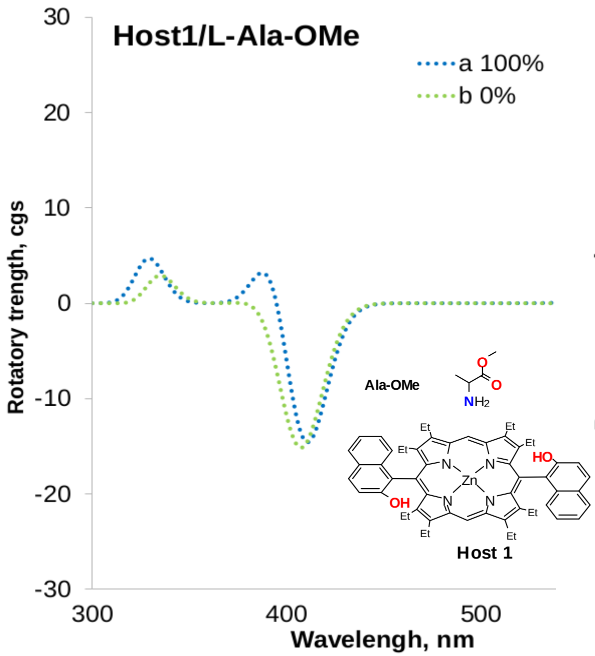
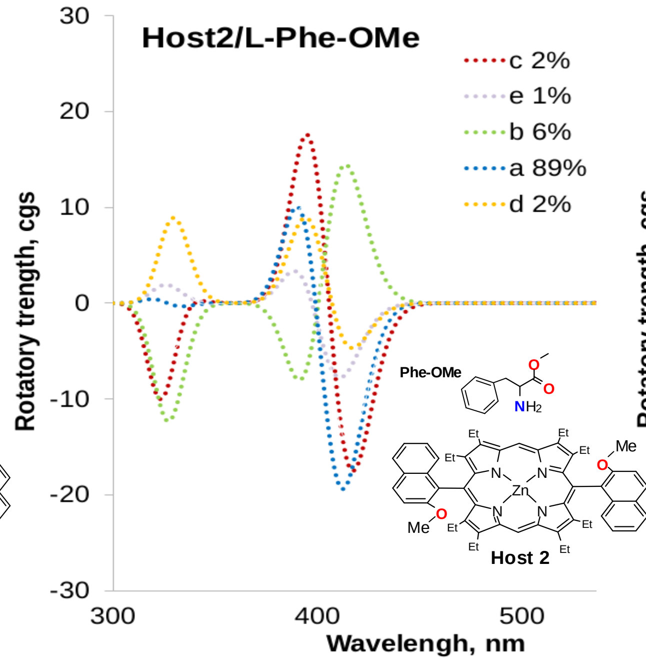
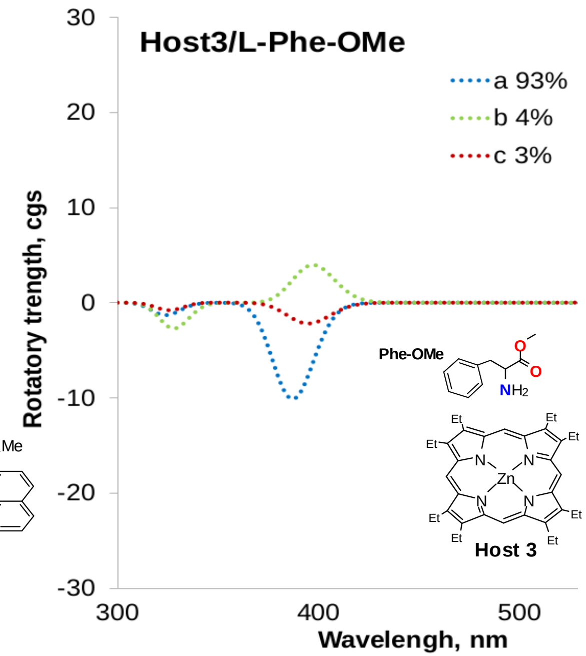
Monoporphyrins



Influence of other chromophores (guest)

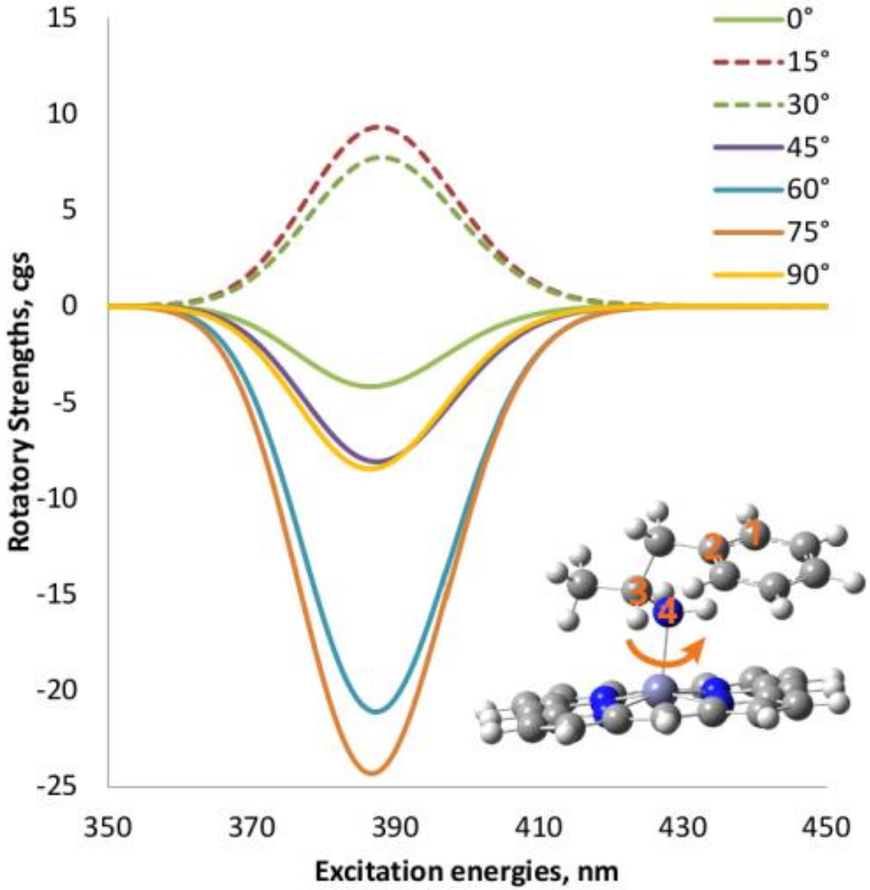


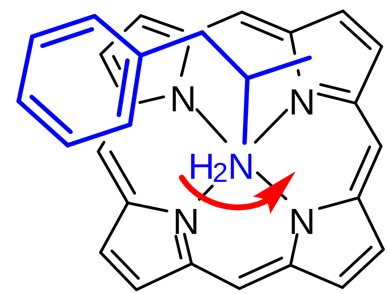




Osadchuk, I.; Borovkov, V.; Aav, R.; Clot, E. *Phys. Chem. Chem. Phys.* **2020**, *22*, 11025–11037.

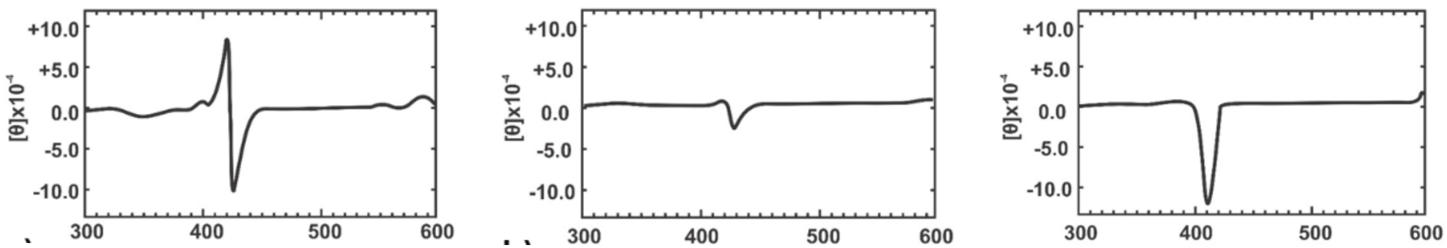
Influence of other chromophores (guest)

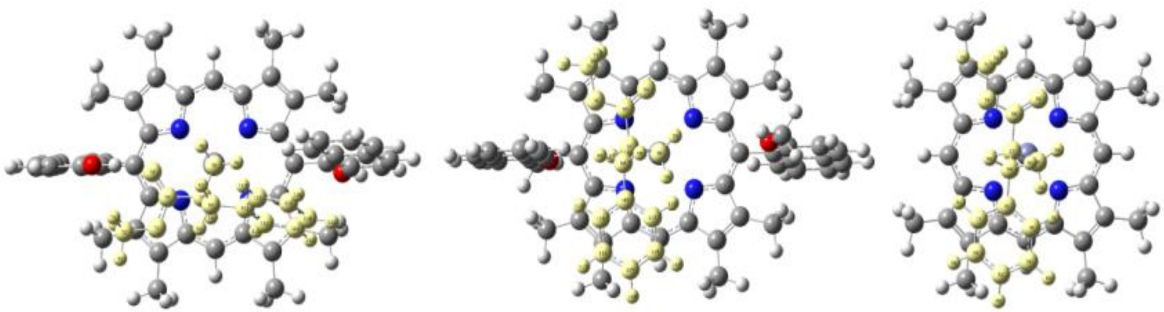




Relative position of a guest's chromophore determinates the sign of the CD signal.

Influence of other chromophores (guest)

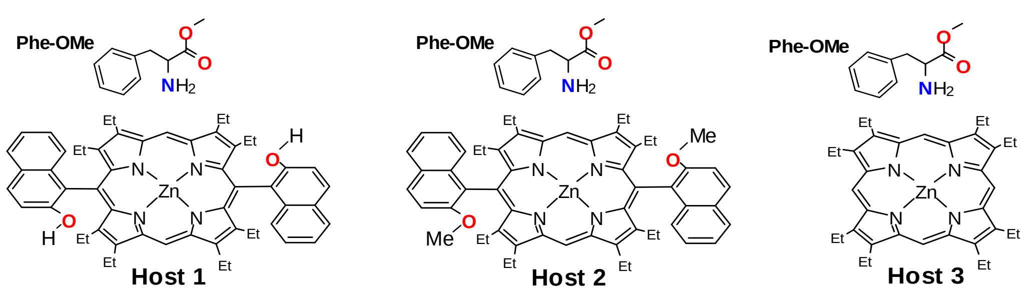




Host 1/Phe-OMe

Host 2/Phe-OMe

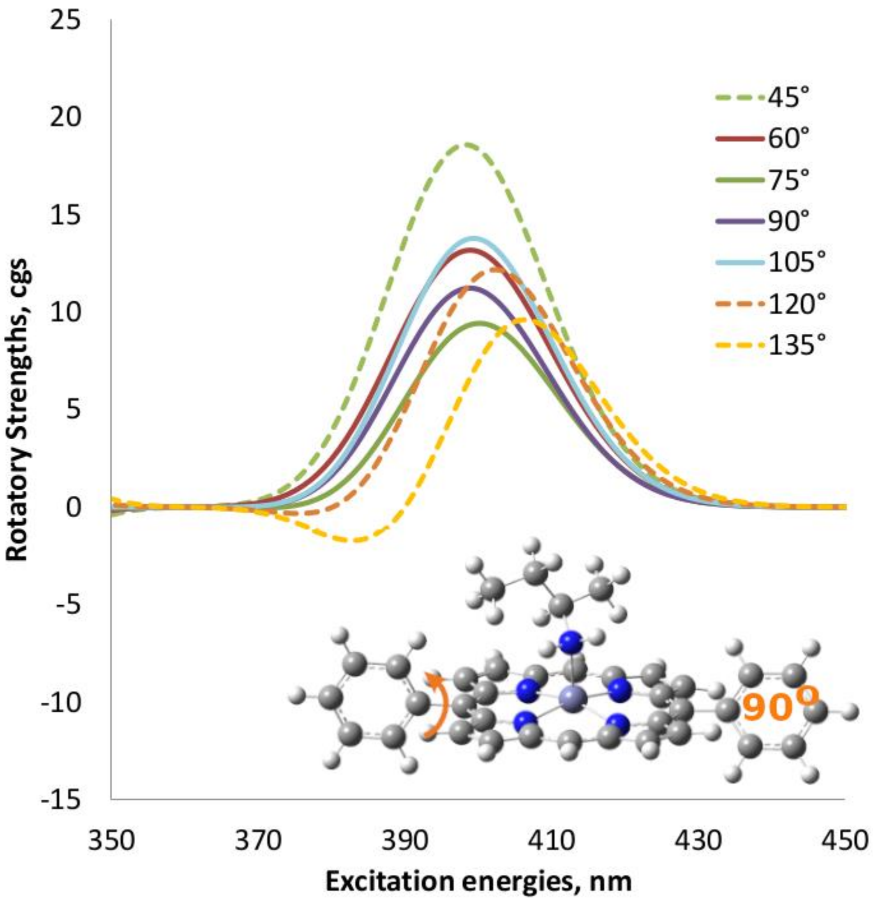
Host 3/Phe-OMe

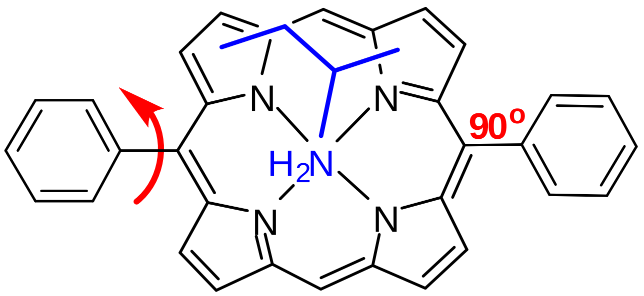


- Vary of hosts causes change of a dominant conformers, and, as a consequence, change in position of a guest's chromophore.
- Conformation of a guest determines position of peripheral substituents.

- Mizutani, T.; Ema, T.; Yoshida, T.; Kurodo, Y.; Ogoshi, H. *Inorg. Chem.* **1993**, *32*, 2072–2077.
- Osadchuk, I.; Borovkov, V.; Aav, R.; Clot, E. *Phys. Chem. Chem. Phys.* **2020**, *22*, 11025–11037.

Influence of other chromophores (peripheral substituents)

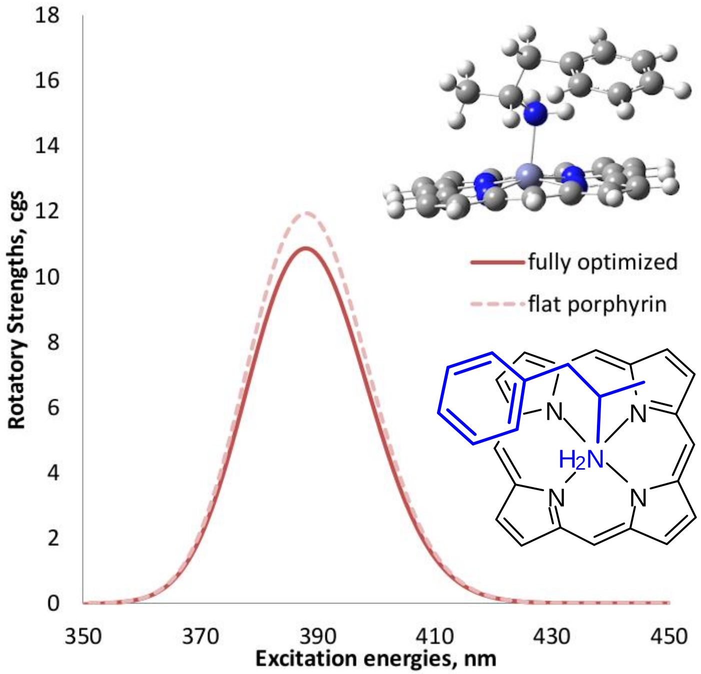


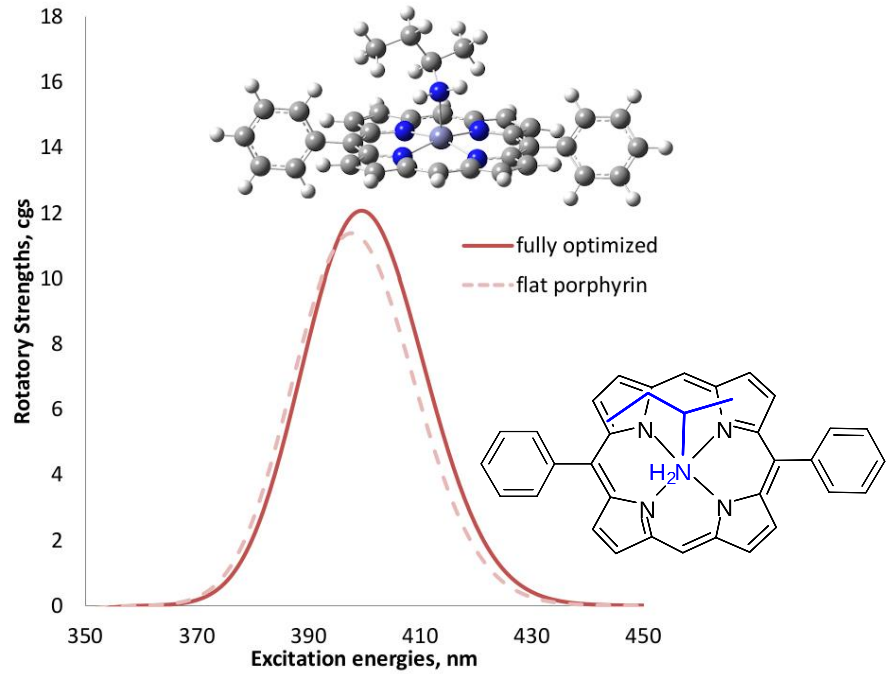


Position of a peripheral porphyrin substituent (chromophoric) is responsible for the split of the CD signal.

- Nagai, M.; Mizusawa, N.; Kitagawa, T.; Nagatomo, S., *Biophys. Rev.* **2018**, *10*, 271–284.
- Šebek, J.; Bouř, P., *J. Phys. Chem. A* **2008**, *112*, 2920–2929.
- Kobayashi, N.; Higashi, R.; Titeca, B. C.; Lamote, F.;Ceulemans, A., *J. Am. Chem. Soc.* **1999**, *121*, 12018–12028.

Influence of porphyrin plane distortion

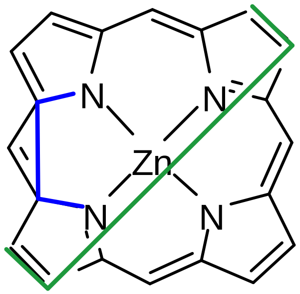




Distortion of porphyrin plane cases B-band shift, but the dependence is nonlinear.

- Graves, A. B.; Graves, M. T.; Liptak, M. D, *J. Phys. Chem. B* **2016**, *120*, 3844–3853.

Porphyrin plane distortion

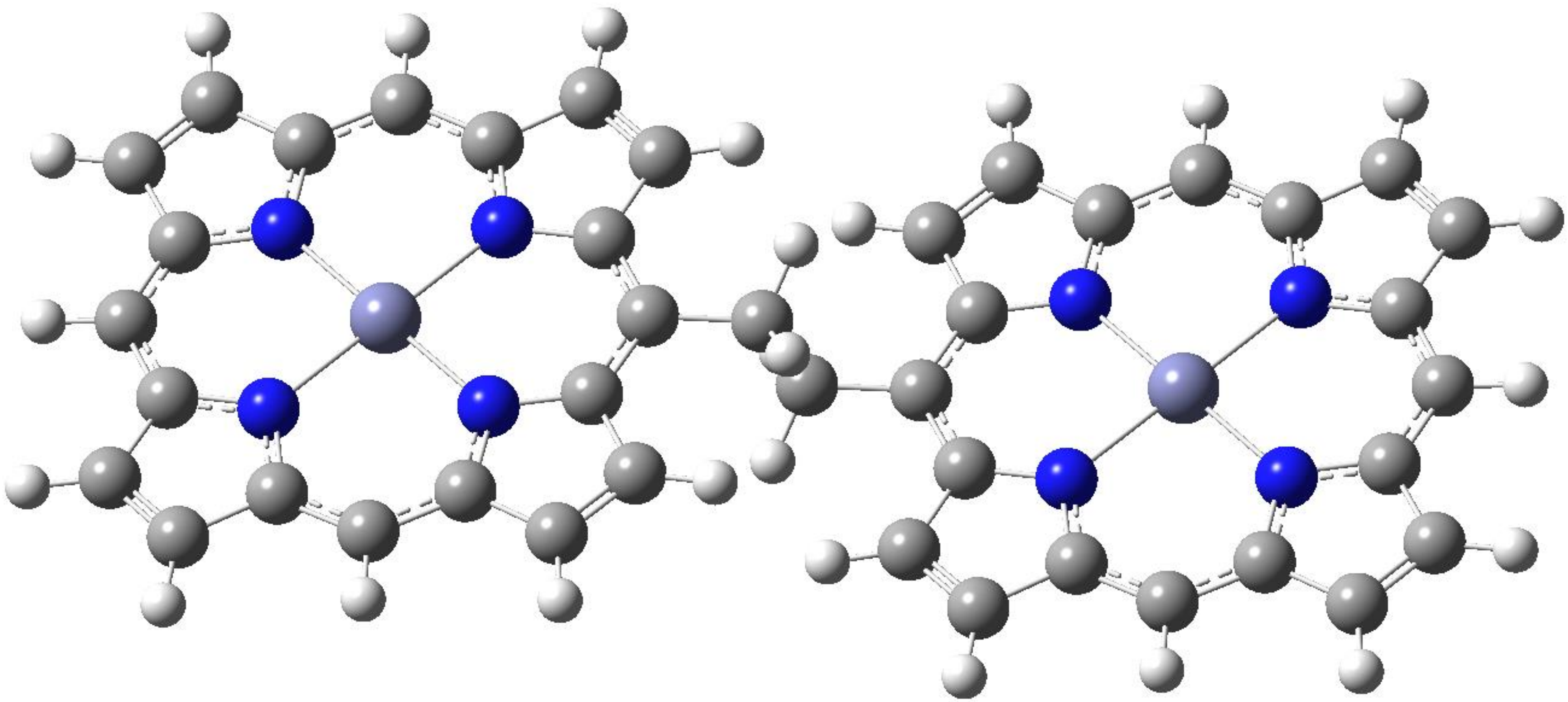


	C_β-C_β-C_β-C_β		N-Cα-Cα-N			
Supramolecule1	0,5	-0,5	1,0	0,1	1,5	-2,4
Supramolecule2	2,3	-1,0	0,3	-1,3	3,1	-2,5

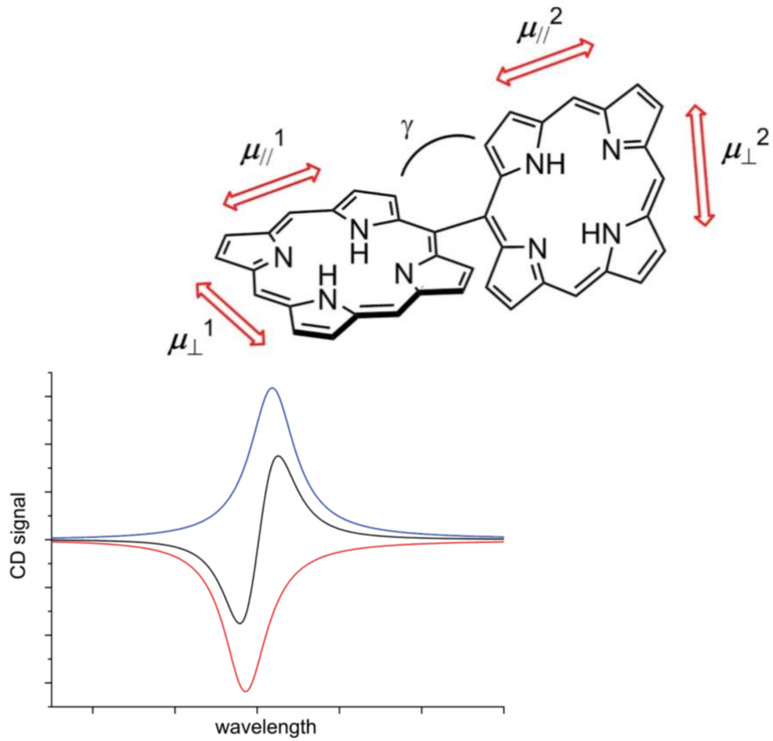
Guest	Host	C_β-C_β-C_β-C_β		N-Cα-Cα-N			
Ala-OMe	**1**	7,3	-4,8	-2,2	-0,3	-2,8	6,8
Leu-OMe	**1**	10,8	-7,7	-2,1	2,3	-3,5	5,7
Phe-OMe	**1**	1,7	-2,3	-4,5	5,6	-4,5	6,4
Phe-OMe	**2**	0,6	-0,3	0,0	-1,2	-0,5	2,0
Phe-Ome	**3**	0,6	-0,3	0,0	-1,2	-0,5	2,0

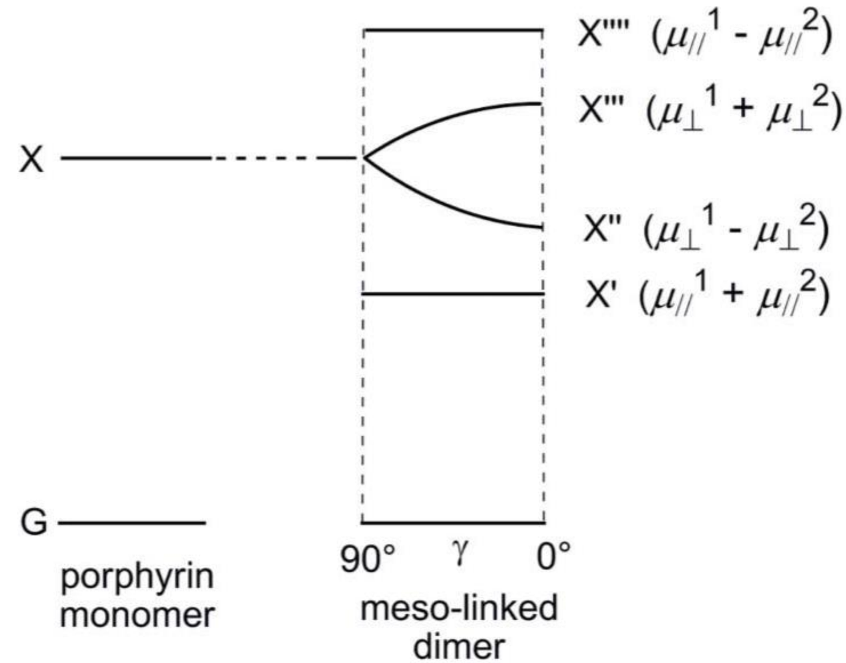
Osadchuk, I.; Borovkov, V.; Aav, R.; Clot, E. *Phys. Chem. Chem. Phys.* **2020**, *22*, 11025–11037.

Bisporphyrins



Exciton coupling

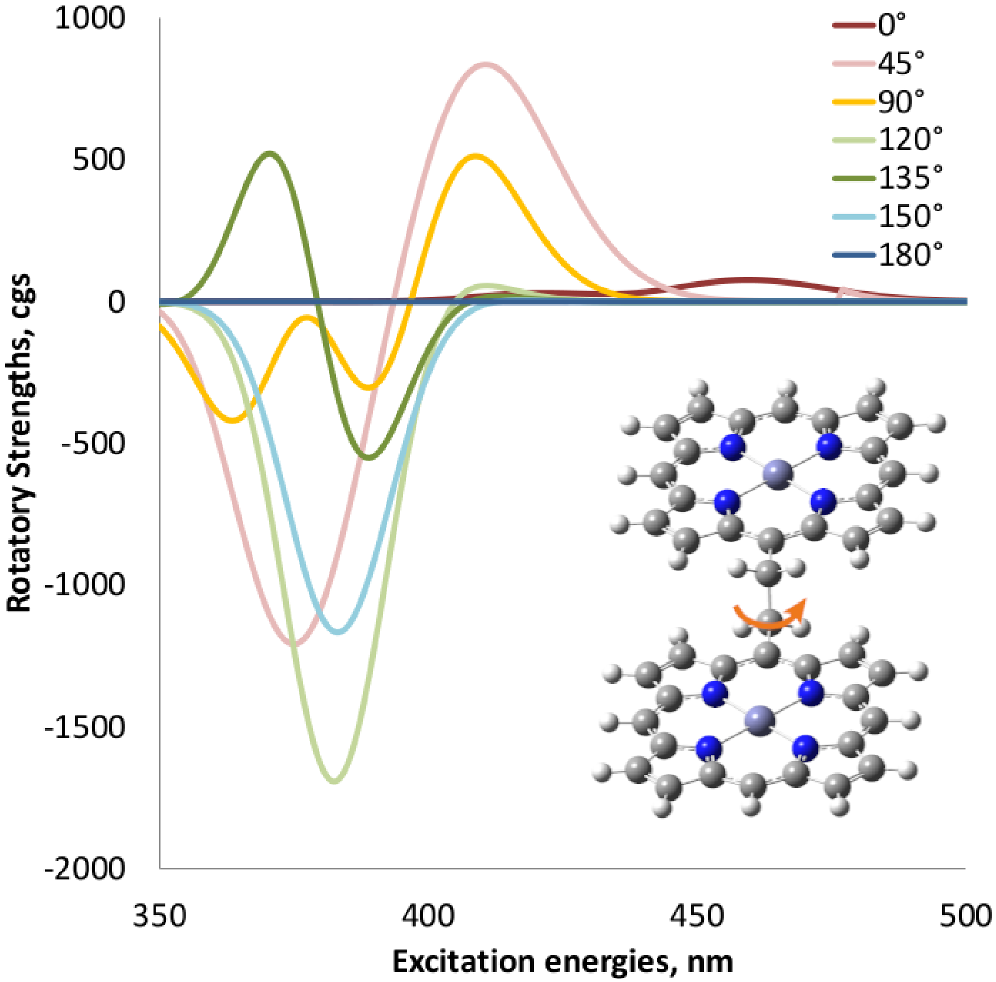




"In the simplest case of exciton coupling, a pair of degenerate chromophores interacts to give a set of two nondegenerate excited states. These excitonic states are linear combinations of the unperturbed excited state of the individual chromophores. One excitonic state lies at higher energy than the original excited state, while the other lies at lower energy."

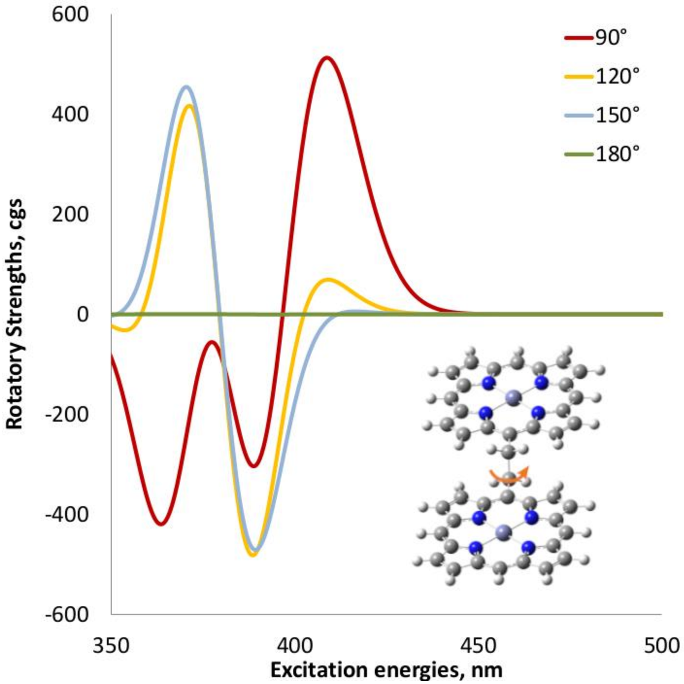
Telfer, S. G.; McLean, T. M.; Waterland, M. R., *Dalt. Trans.* **2011**, *40*, 3097–3108.

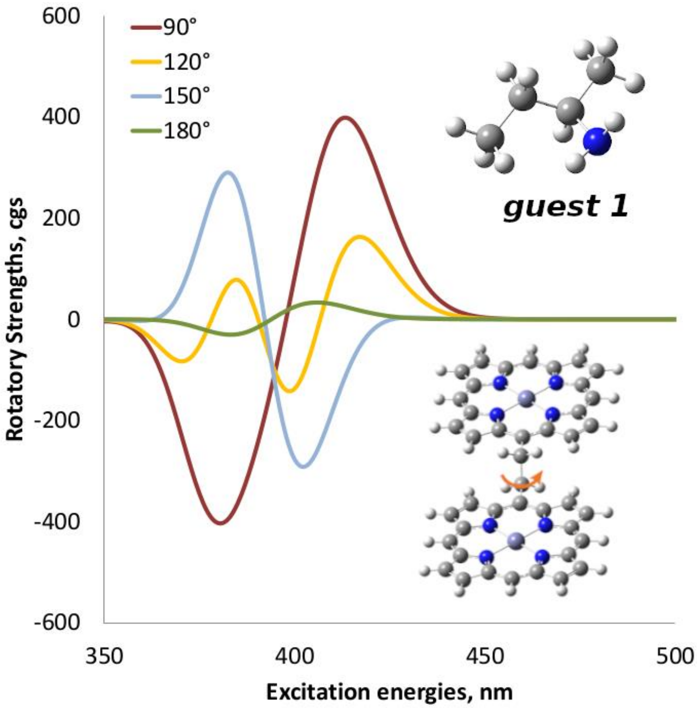
Influence of position of porphyrin subunits



Change in the orientation of the of the porphyrin sub-units leads to the appearance of CD spectra even in the absence of a chiral ligand, since the molecule adopt directional helicity.

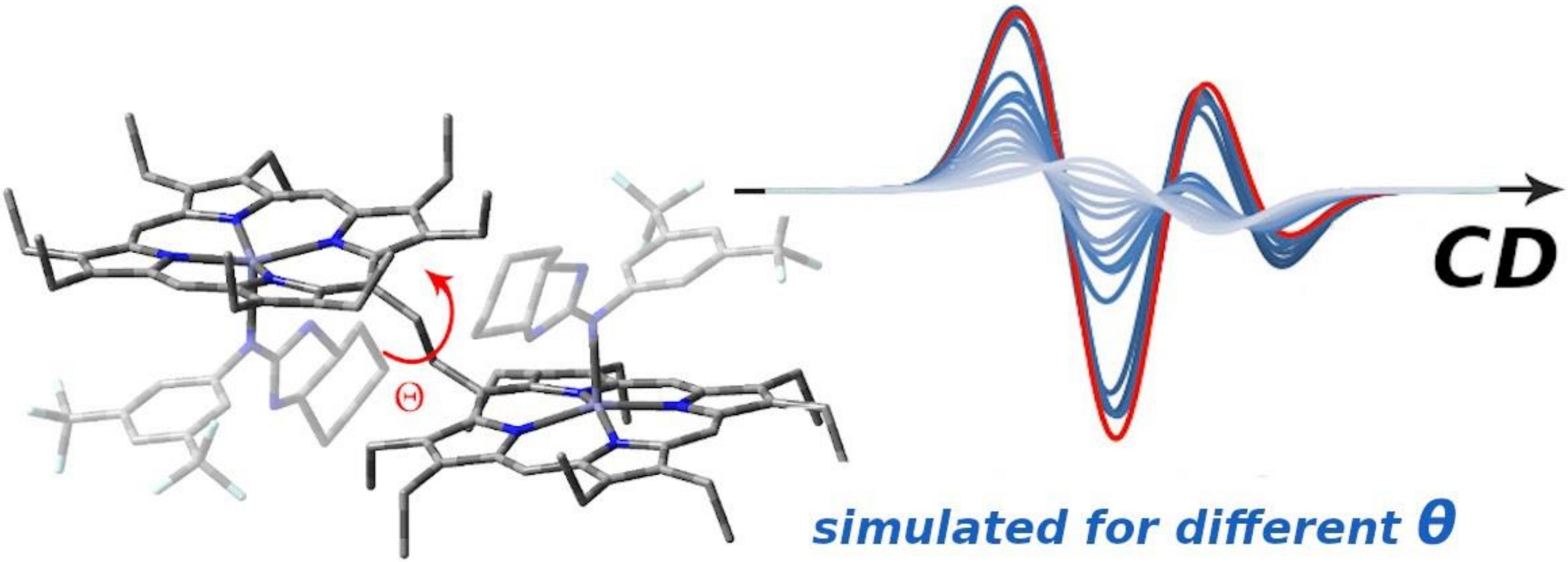
Influence of chiral guest





By binding of a chiral guest bisporphyrin becomes chiral that results in significantly change in the shape of the CD spectra and shifts bands to the lower energy.

Influence of position of porphyrin subunits



- *Osadchuk, I.; Konrad, N.; Truong, K.-N.; Rissanen, K.; Clot, E.; Aav, R.; Kananovich, D.; Borovkov, V.; Symmetry* **2021**, *13*(2), 275
- Dhamija, A.; Saha, B.; Chandel, D.; Malik, H.; Rath S.P.; *Inorg. Chem.* **2020**, *59*, 1, 801–809.
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- Lu, H.; Kobayashi, N.; *Chem. Rev.* **2016**, *116*, 6184–6261
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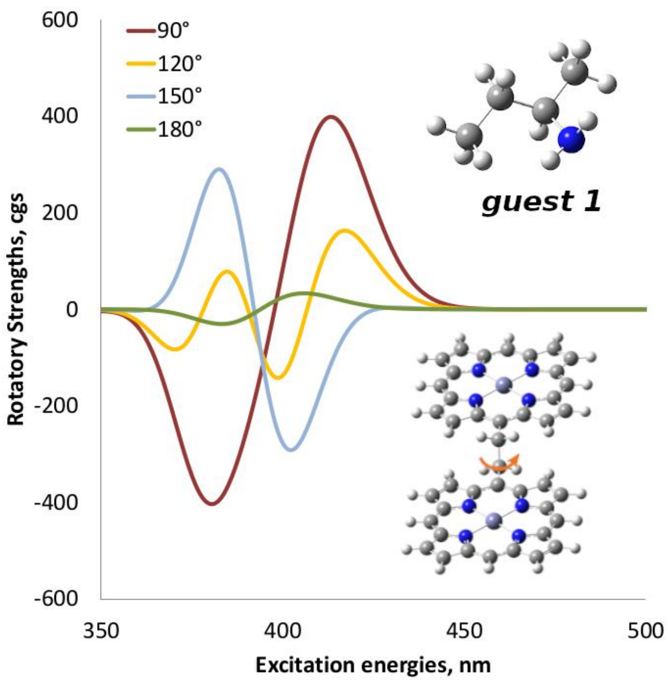
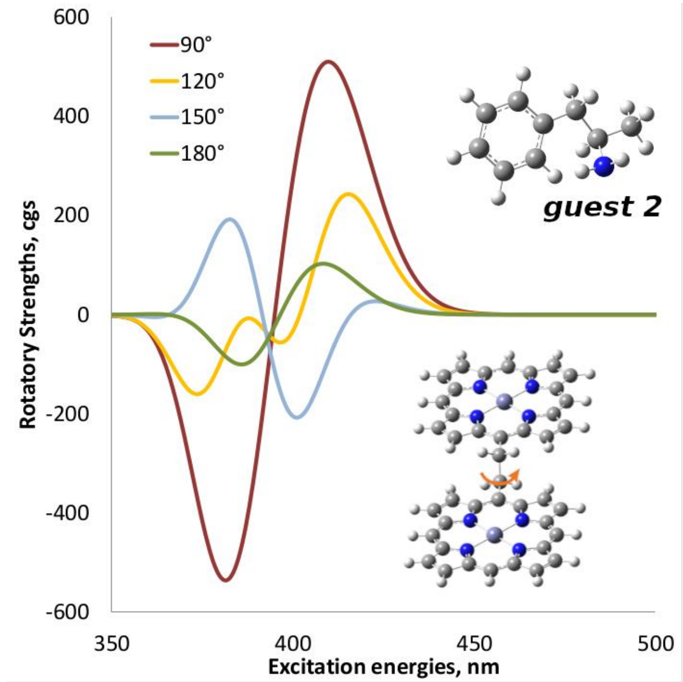
Influence of chiral guests

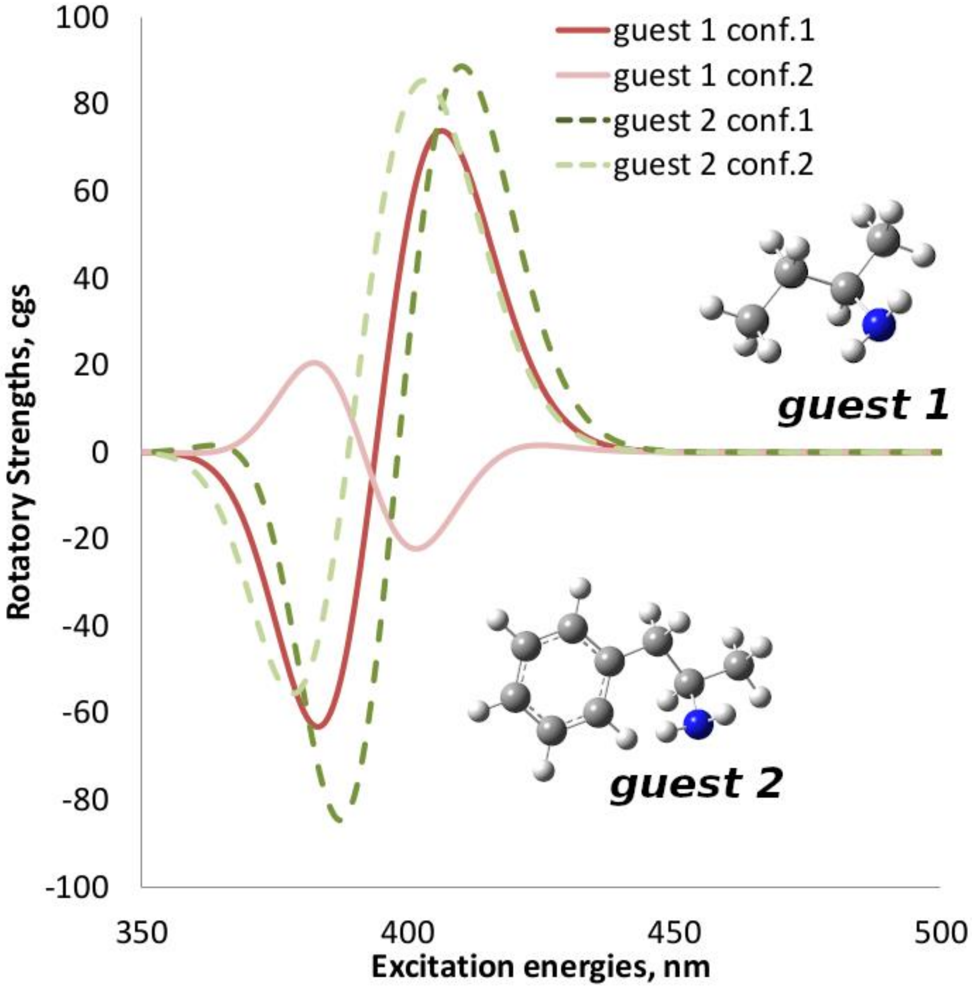




CD spectra with varying guests are similar by shapes and differ by intensities, as long as the position of the porphyrin subunits remains similar.

Chmielewski, P.J.; Siczek, M.; Stępień, M. *Chem. A Eur. J.* **2015**, *21*, 2547–2559.
Borovkov, V. V.; Hembury, G. A.; Yamamoto, N.; Inoue, Y.; *J. Phys. Chem. A,* **2003**, *107*, 41, 8677–8686

Influence of conformation



- Depending on adopt conformation spectra can differ significantly due to different position of porphyrin subunits determined by steric hindrance.
- The guest's chro-mophore plays a minor role.

Summary

Sensors based on monoporphyrins:

- Relative position of a guest's chromophore determinates the sign of the CD band;
- Position of a peripheral porphyrin substituent (chromophoric) is responsible for a split of CD signal;
- Small distortion of porphyrin plane does not cause significant changes in CD spectra.

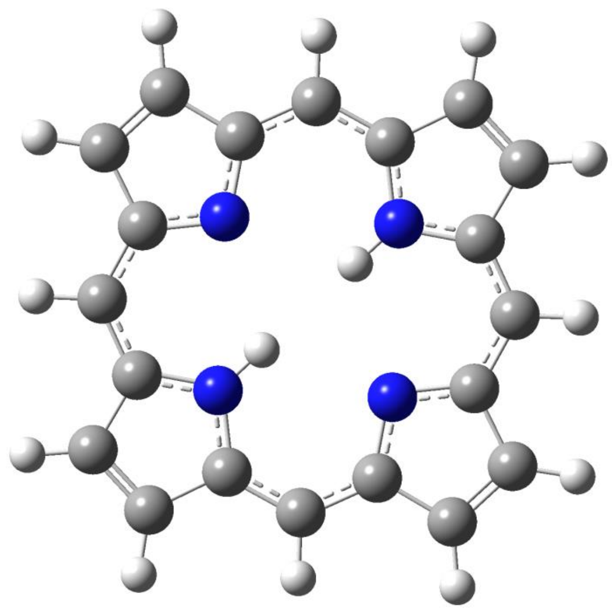
Sensors based on bisporphyrins:

- Change in a position of porphyrin subunits determinates the sign and the shape of the CD spectra;
- By binding of a chiral guest bisporphyrin becomes chiral that results in significantly change in the shape of the CD spectra and shifts bands to the lower energy;
- CD spectra with varying guests are similar by shapes and differ by intensities, as long as the position of the porphyrin subunits remains similar;
- A guest's chromophore plays a minor role.

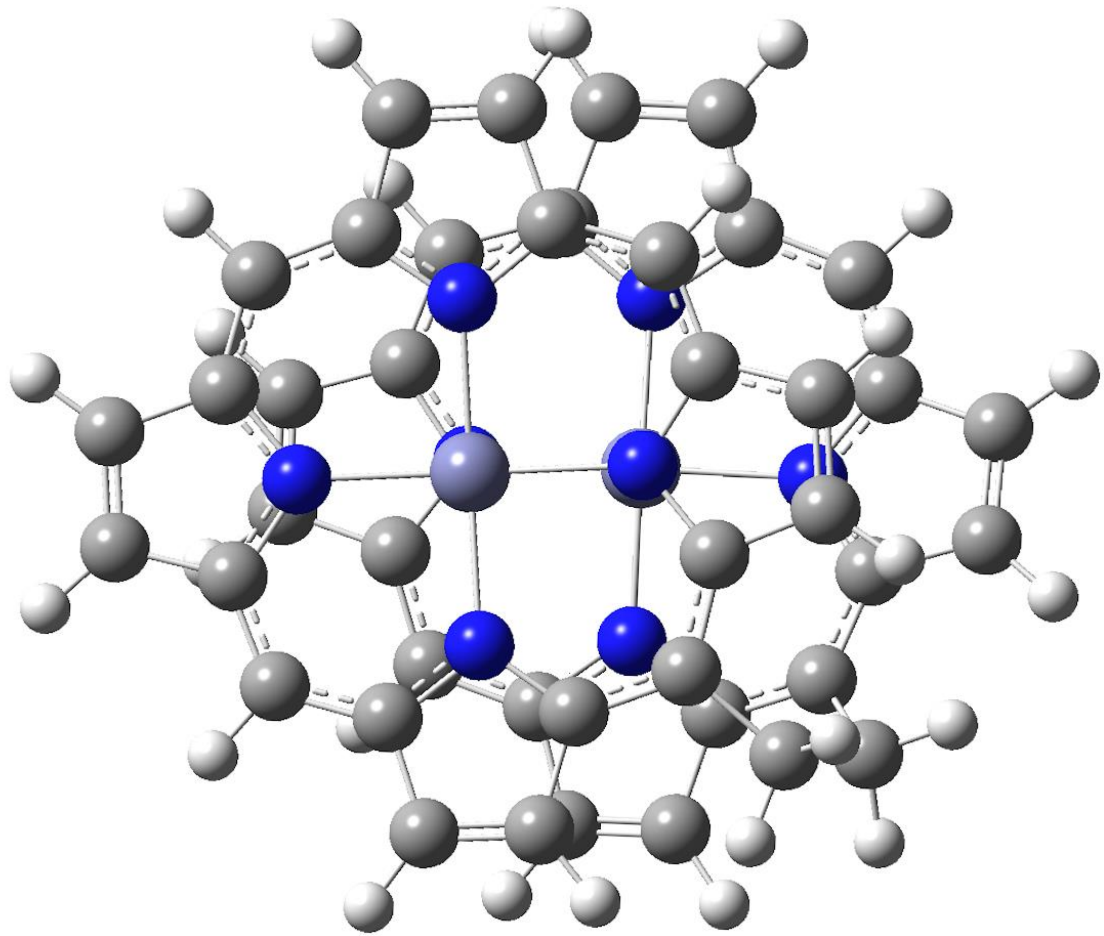
Acknowledgments

- Prof. V. Borovkov
- Prof. T. Tamm

- HPC cluster at Tallinn University of Technology
- The Estonian Research Council grant PUTJD749



Thank you!



Questions?