Looking for simplified molecular-reaction coordinates from computation data

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Case 1: optical response of BODIPY environment sensors

- Boron-dipyrromethene (with central rotation group) and variants
- Fluorescence lifetime can be calibrated to reflect variations in environment properties (viscosity, polarity, temperature)[1]
- Promising for medical uses and *in vivo* imaging

Goal: to approximate a reaction coordinate of optical excitation

Computation type: TD-DFT semi-constrained scan (*Gaussian* 16)
- BODIPY core with different rotation groups
- M06-2X / *cc-pVDZ*, C-PCM solvent (toluene) (0,5–2° steps)
  (TD-DFT – time-dependent density functional theory)

**Challenge**: single rotation angle does not preserve symmetry

φ_L = **+5,5** °
φ_R = **−6,0** °
out-of-plane $_U$ = 2,8 °
out-of-plane $_D$ = 7,7 °
$\theta \approx 135$ °
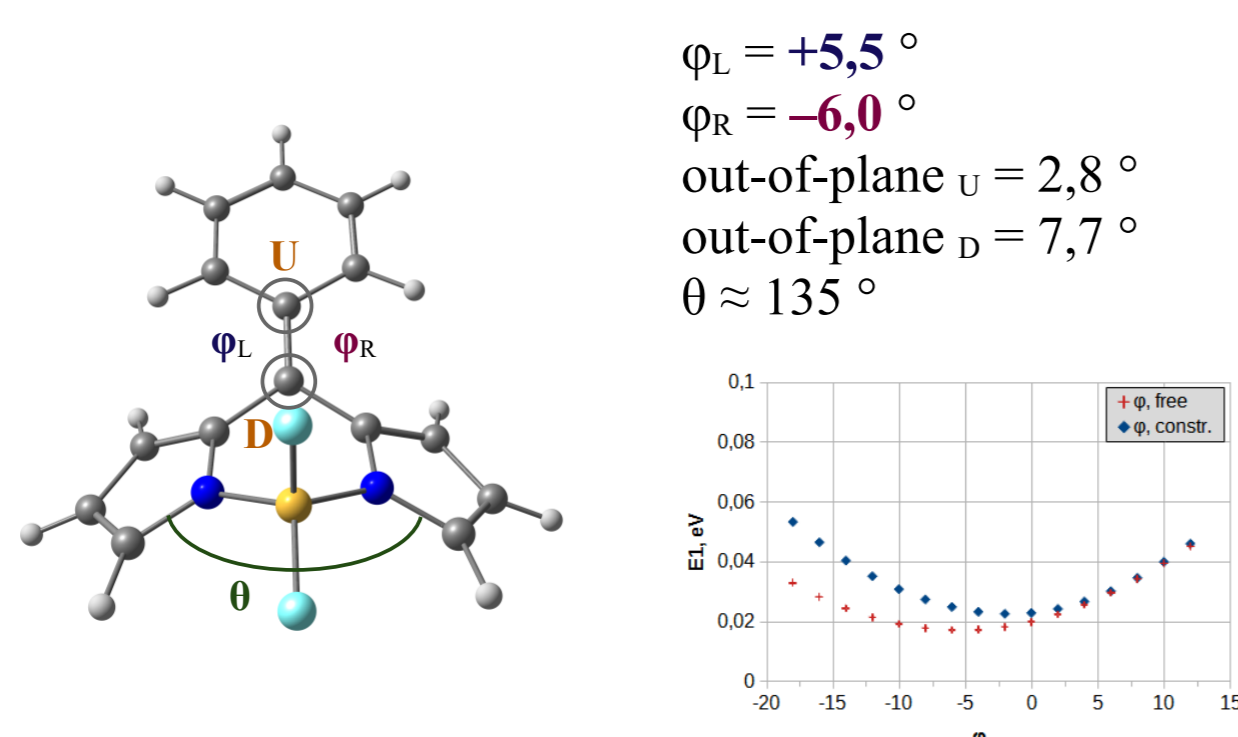
Analysis

- First-order **reaction coordinate** φ_C is defined here as
  $\varphi_C = \frac{1}{2} (\varphi_R + \varphi_L)$
- Validated for viscosity-dependent fluorescence lifetime (FLIM) response calibration based on excited-state PES[1,2]
  (PES – potential-energy surface)

Results

- Correct estimation of parallel (0°) and cross (-90°) symmetry for the appropriate vinyl-based and phenyl rotation groups
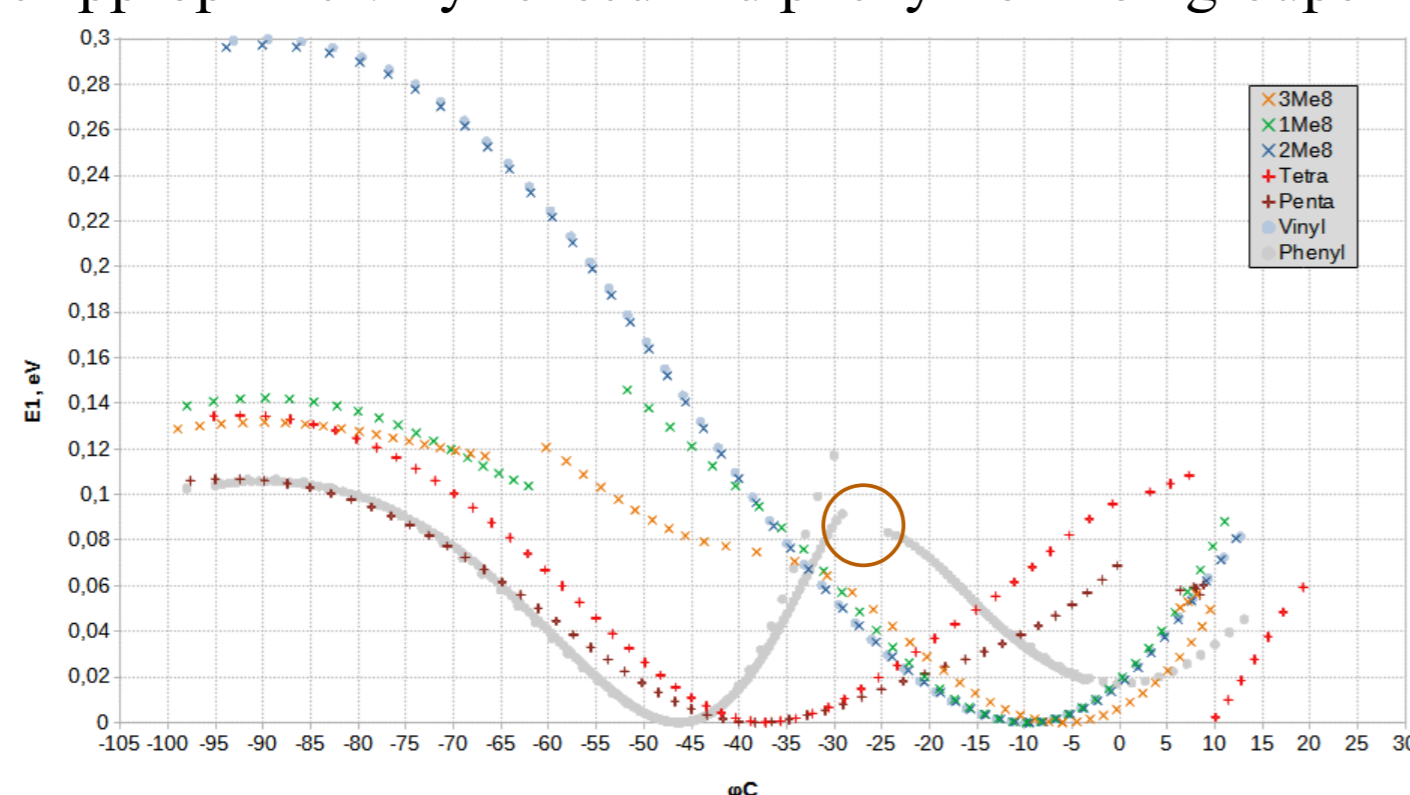
Outlook

- Certain regions are difficult to sample using φ_C (*see marking*)
- Data analysis for more complex reaction coordinate is ongoing

Case 2: spontaneous structure of TPPS$_4$ oligomers

- 5,10,15,20-tetrakis(4-sulfonatophenyl)porphyrin and variants
- Known to self-aggregate[3] and self-organize into chiral structures[4] depending on the surrounding properties
- Promising for medical uses and molecular self-assembly

Goal: to estimate the emergence of curvature in TPPS$_4$ tetramers

Computation type: MD simulation (*AMBER* 22)
- Z1- and Z2-type linear tetramers
- Single tetramer in water box, 298,15 K, 100 ns (5000 frames)
  (MD – molecular dynamics)

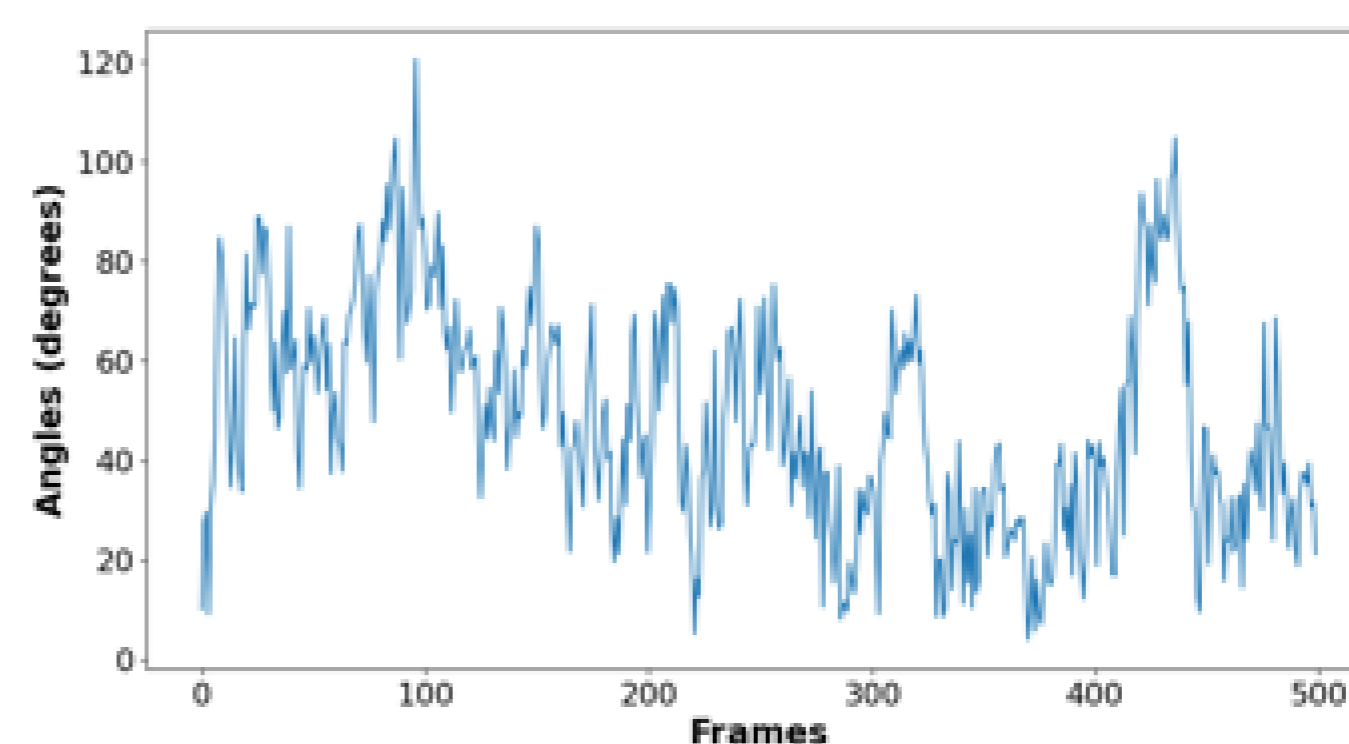**Analysis**

- Intermolecular **curvature angle** α is defined here as
  $\alpha = \arccos \frac{\vec{a}_{12} \cdot \vec{a}_{34}}{|a_{12}| \cdot |a_{34}|}$
  ($\vec{a}_{12}$ and $\vec{a}_{34}$ are vectors between porphyrin ring centers of TPPS$_4$ monomers 1, 2 and 3, 4, respectively)
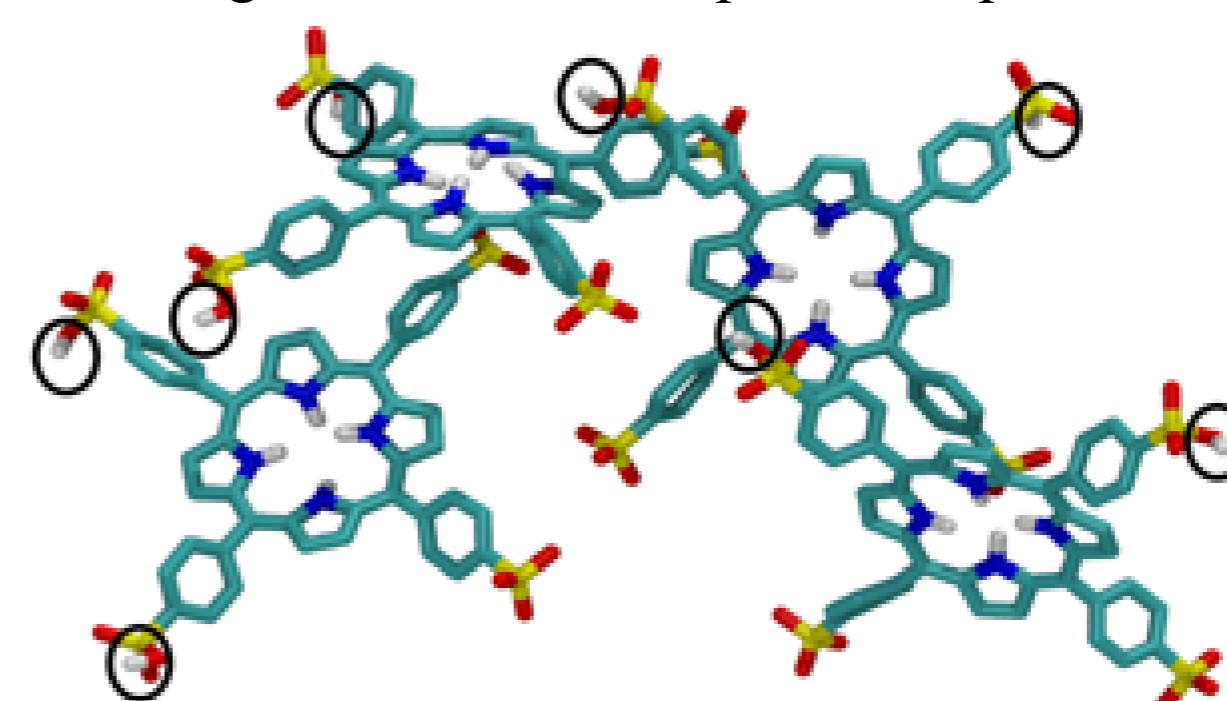- The curvature angles computed along the MD trajectories
  (taking every 10th frame)

Results

- Equilibrium simulation yields slightly curved TPPS$_4$ tetramers

- The curvature angle has short-lived peaks of up to 120° (Z2-type)

Outlook

- Mean curvature angle suggests structures of larger radius
- Stability of peaks over 90° to be checked using TPPS$_4$ octamers

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References

[1] Maleckaitė *et al.*, *Molecules* **27**, 23 (2022)
[2] Toliautas *et al.*, *Chem. Eur. J.* **25**, 10342 (2019)
[3] Baliulytė *et al.*, *AIP Adv.* **13**, 105011 (2023)
[4] Schifino *et al.*, *Mol. Syst. Des. Eng.* **8**, 1512 (2023)