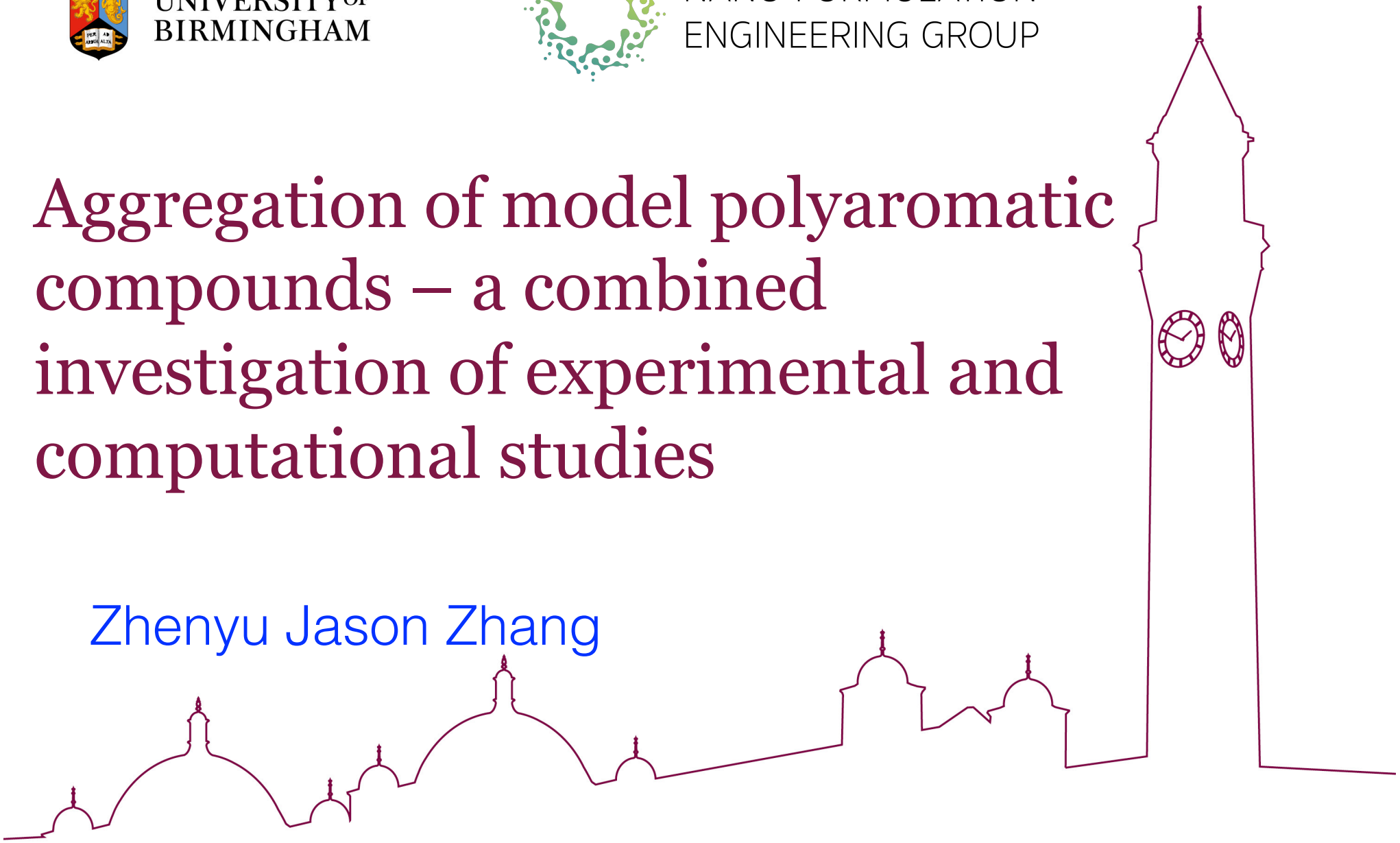
UNIVERSITY OF BIRMINGHAM

NANO-FORMULATION ENGINEERING GROUP

Aggregation of model polyaromatic compounds – a combined investigation of experimental and computational studies



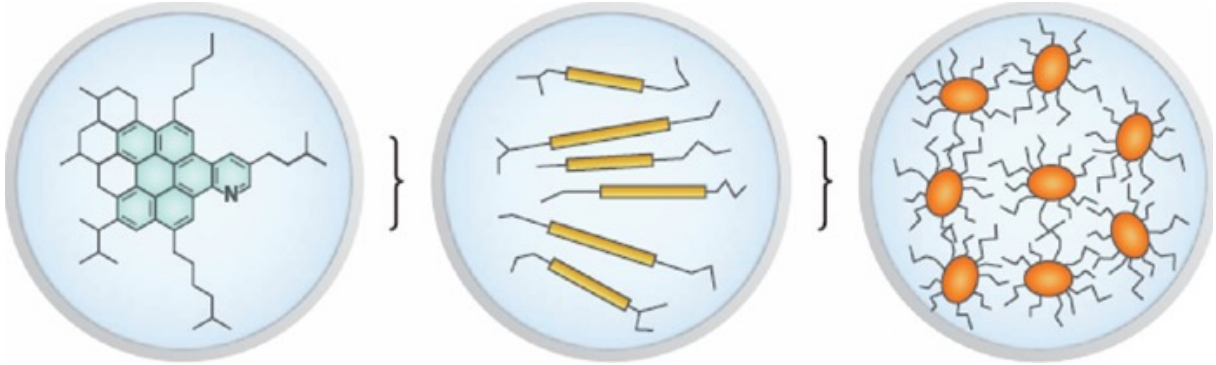
Zhenyu Jason Zhang

z.j.zhang@bham.ac.uk
www.zhenyuzhang.info

School of Chemical Engineering
University of Birmingham

Asphaltene aggregation

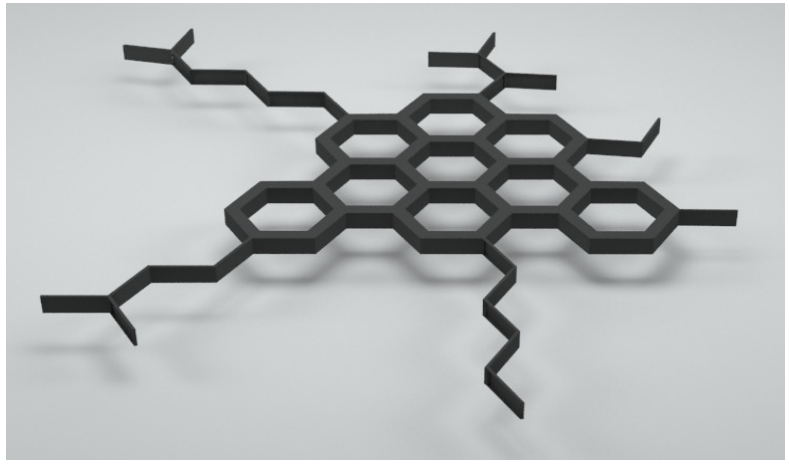
Yen - Mullins Model

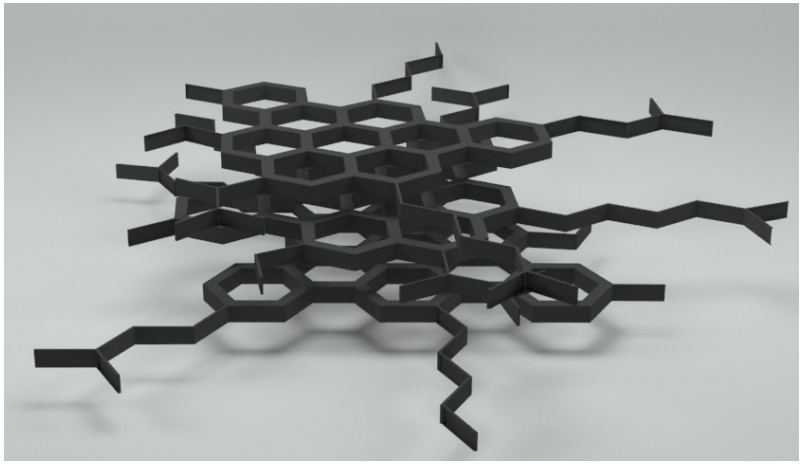


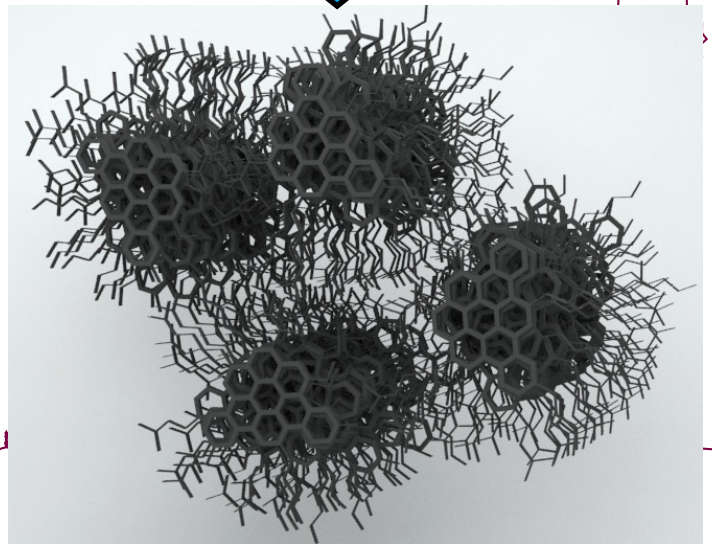
- Implications
- Complex nature
- Research activities
  - Experimental investigation
  - Computational approach

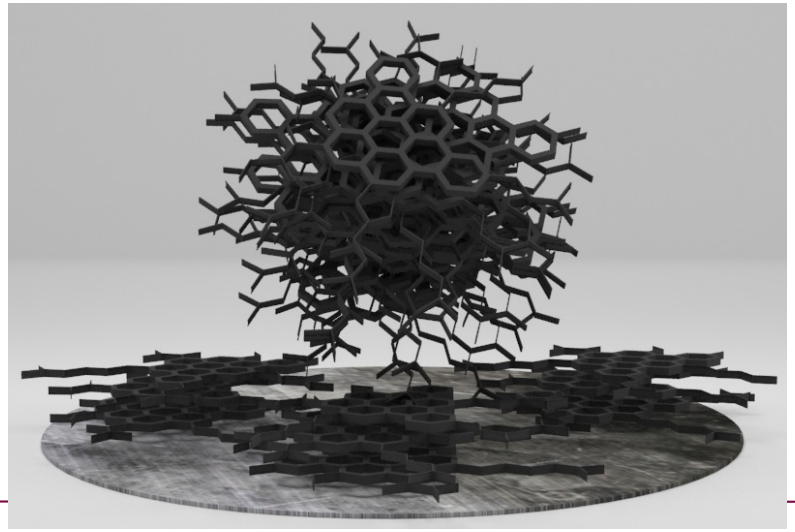
Zhang, Siskin, Gray, Walters, and Rodgers; *Energy Fuels* 2020, 34, 9094

Multiscale phenomena

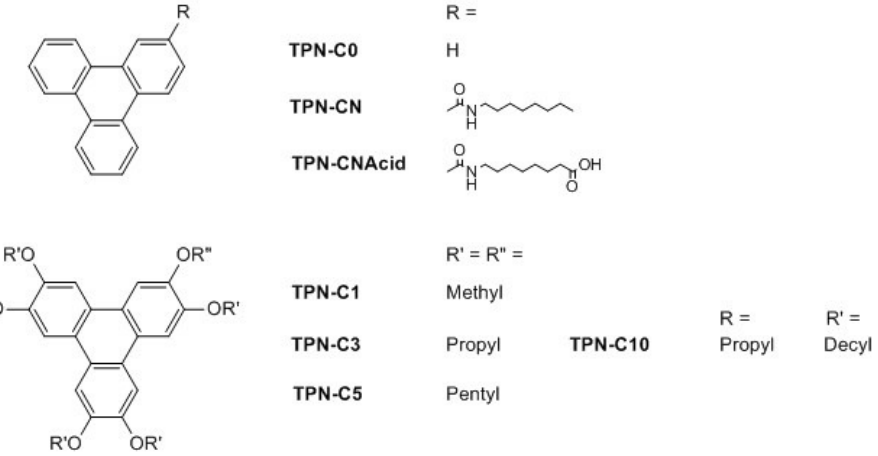




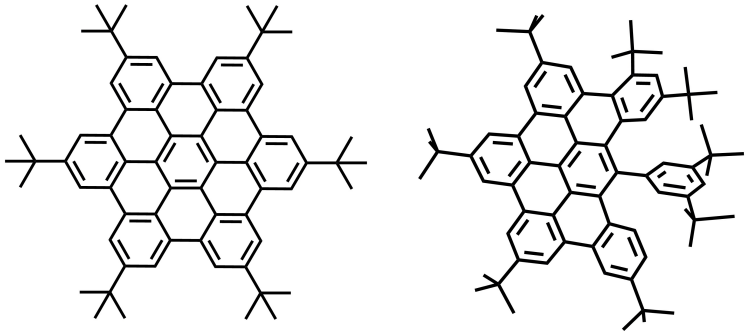




Model PAHs



Triphenylene (TPN) derivatives

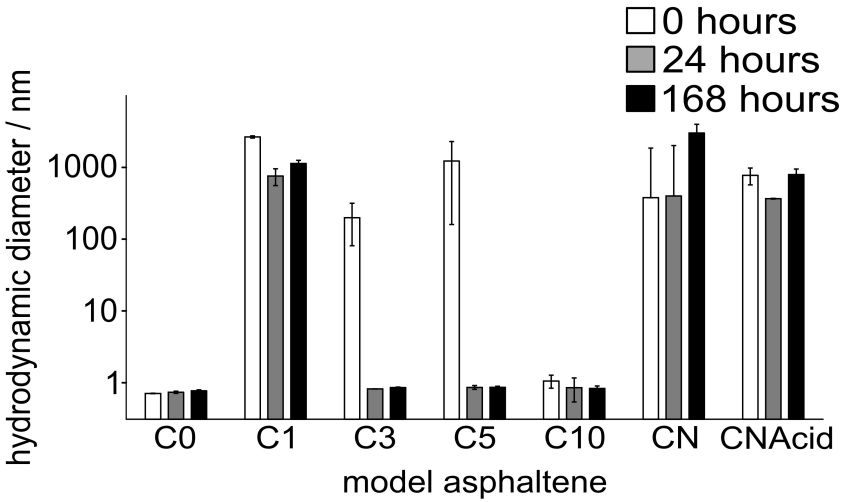


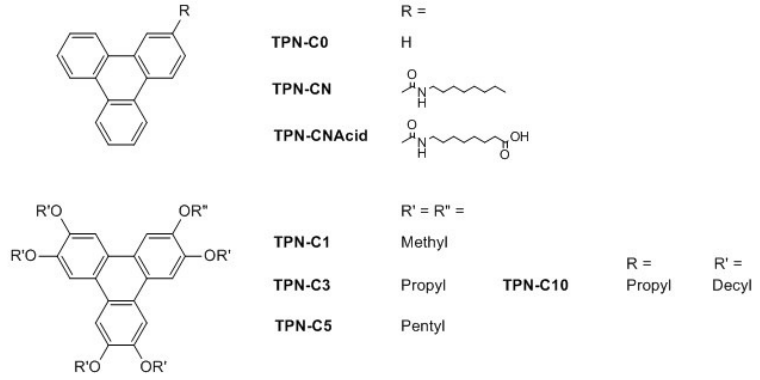
hexa-*tert*-butylhexa-*peri*-hexabenzocoronene (HTBHBC) and derivative

Costa et al. *J. Phys.: Condes. Matter.* 28 (2016) 394002
Simionesie et al. *Colloids Surf., A.* 603 (2020) 125221

Simionesie et al. *Ind. Eng. Chem. Res.* 58 (2019) 20505
Simionesie et al. *Polycyclic Aromat. Compd.* In press

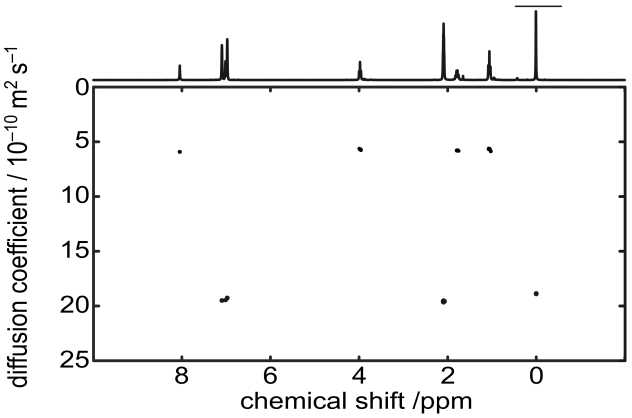
TPN derivatives in toluene

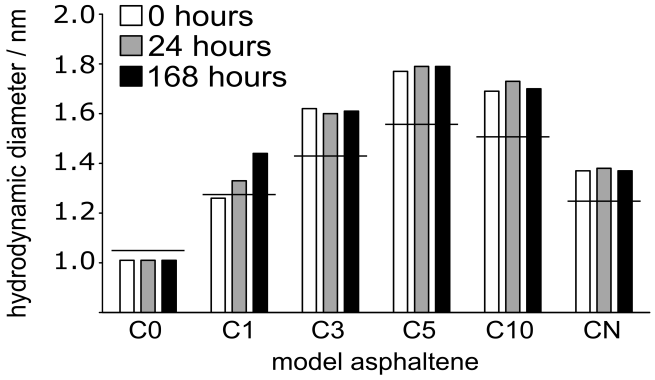


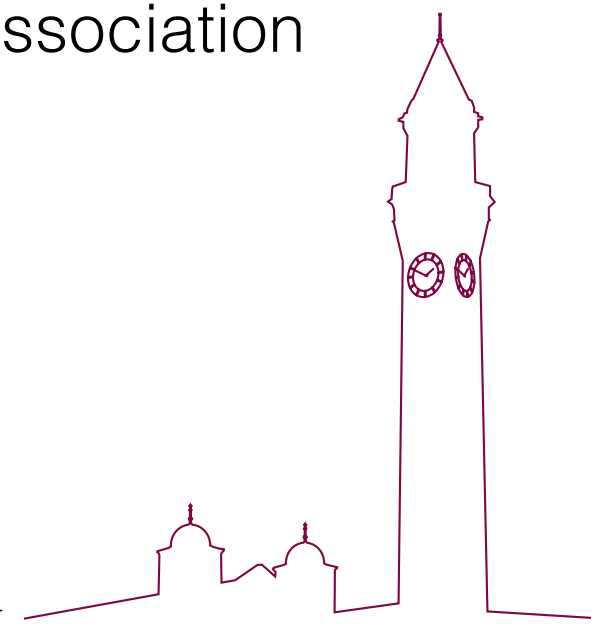


DLS shows initial aggregation, followed by dissociation

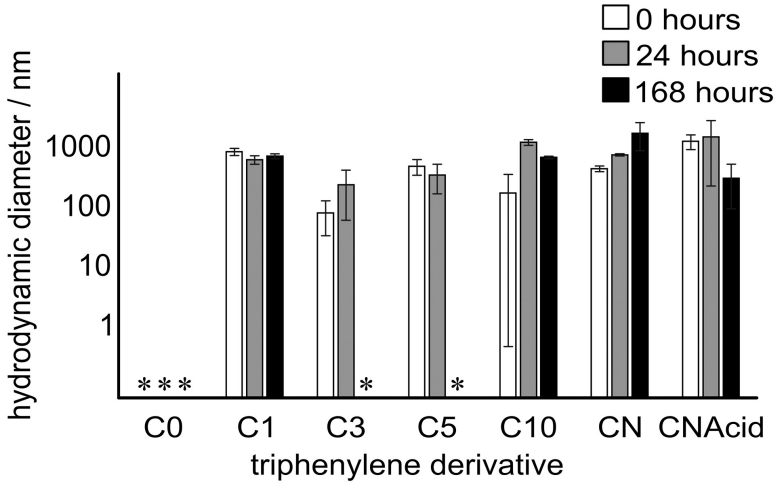
NMR-DOSY shows nanoaggregates

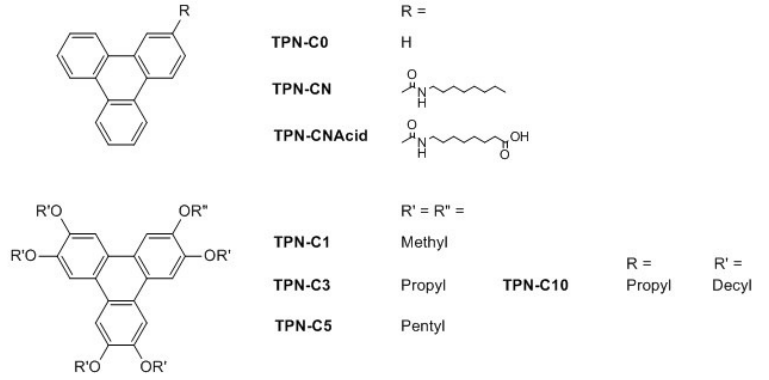






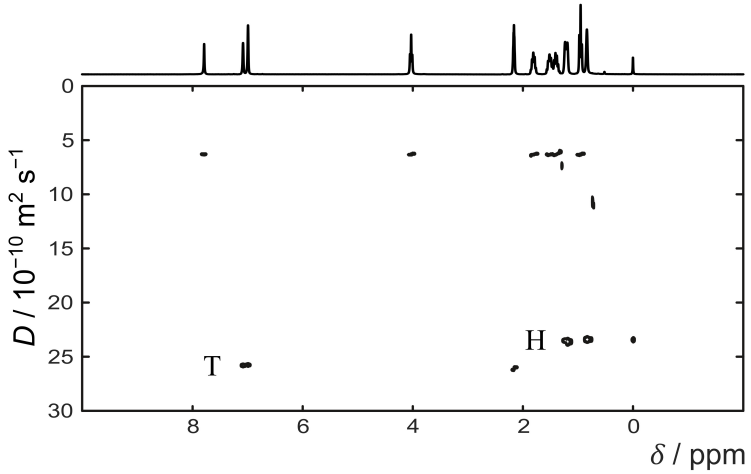
TPN derivatives in toluene/heptane

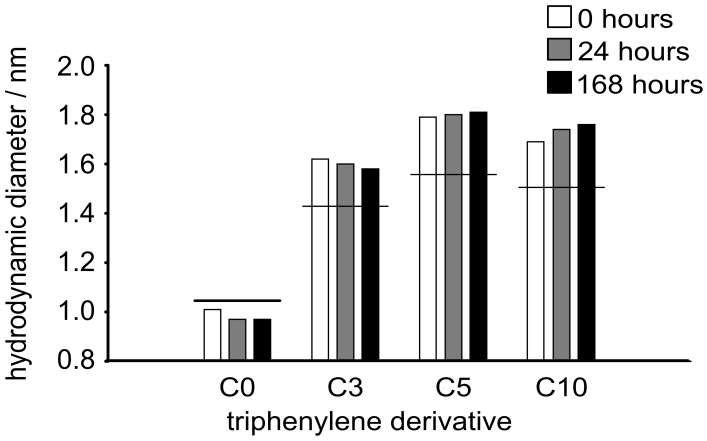




DLS shows immediate aggregation, and there was no dissociation

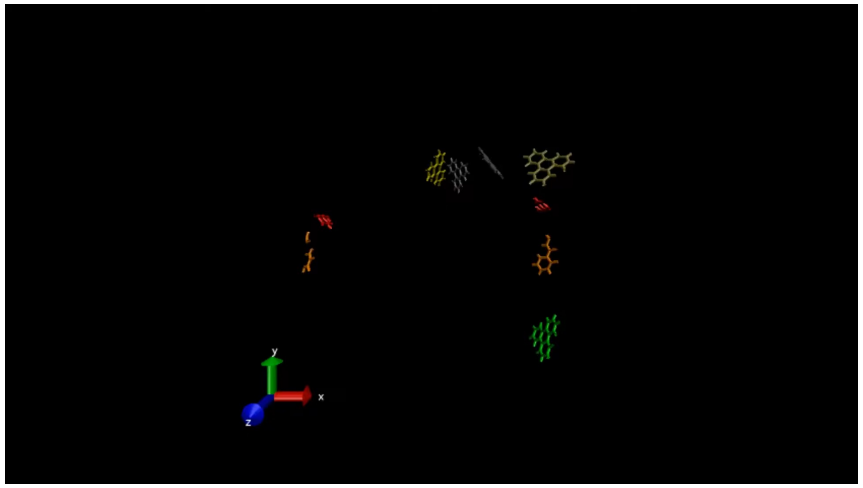
NMR-DOSY shows nanoaggregates



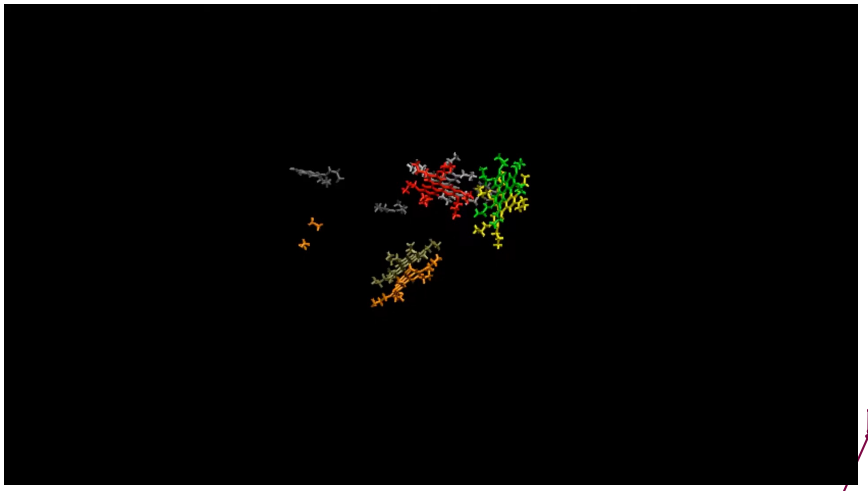


TPN derivatives in toluene

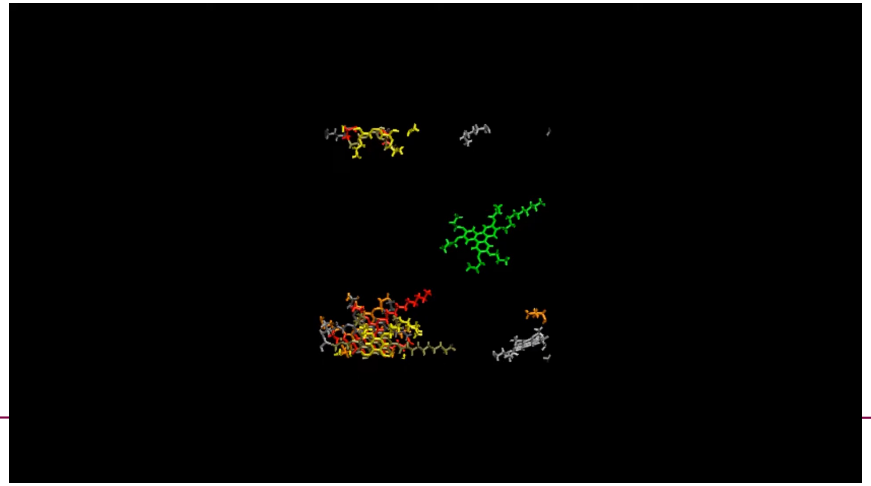
TPN-C0



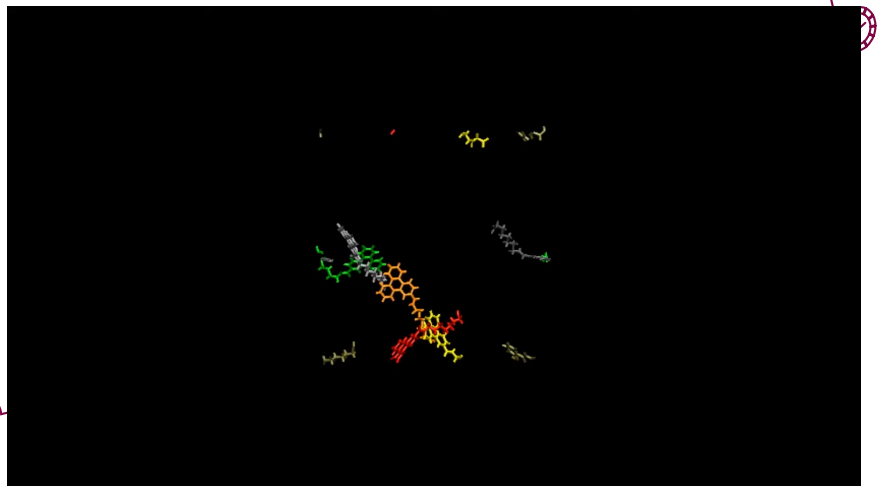
TPN-C3



TPN-C10

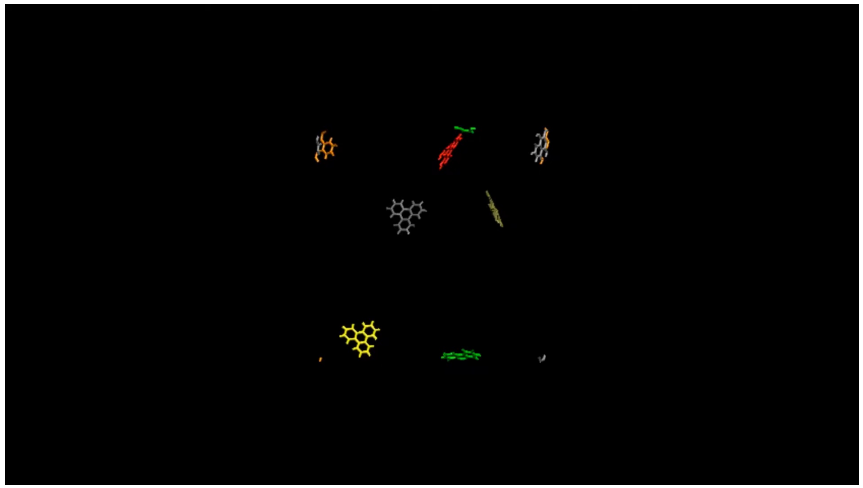


TPN-CNAcid

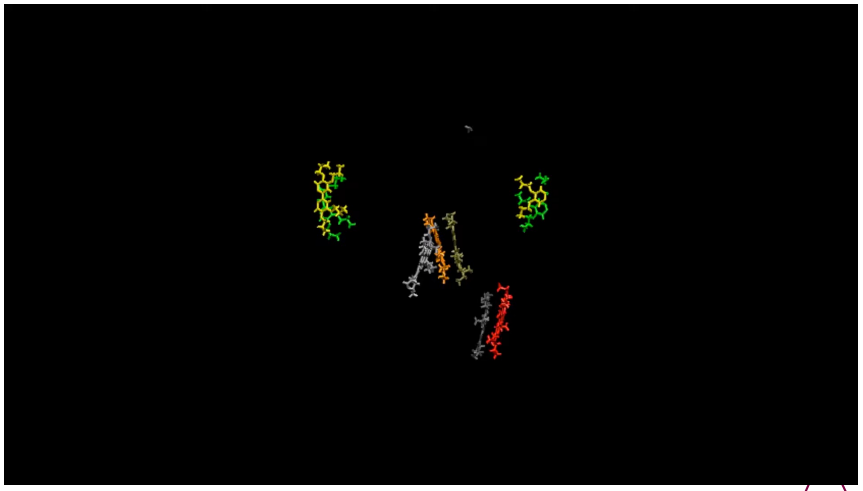


TPN derivatives in toluene/heptane

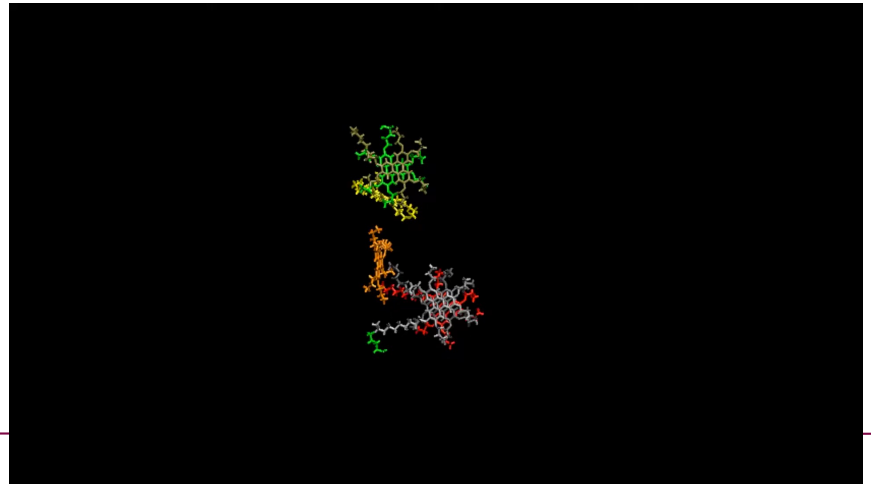
TPN-C0



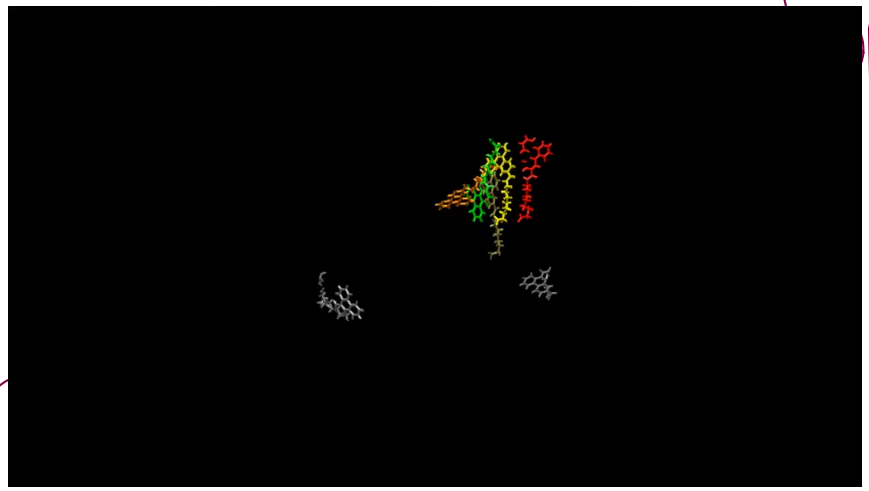
TPN-C3



TPN-C10

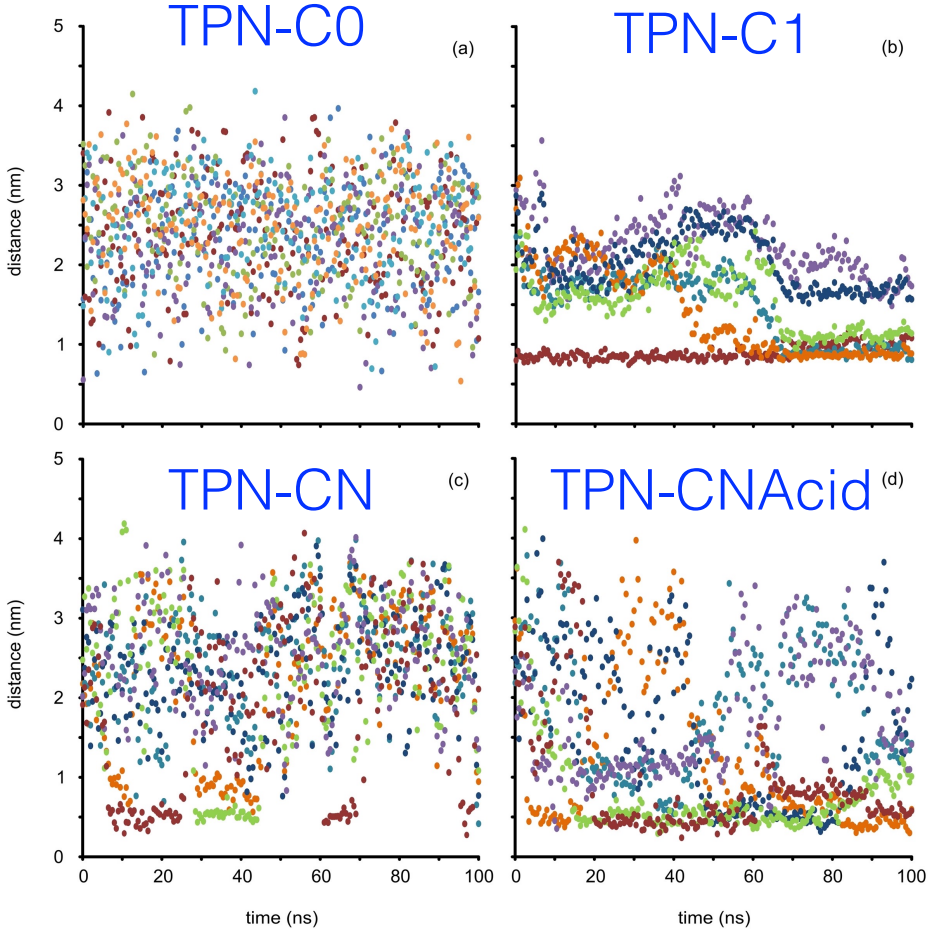


TPN-CNAcid

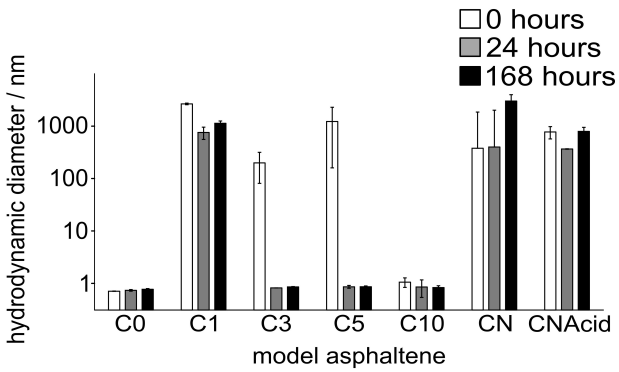


Molecular arrangement in the aggregate

Calculated distances between the centers of mass (COM) for one molecule with the other six molecules, over 100 ns

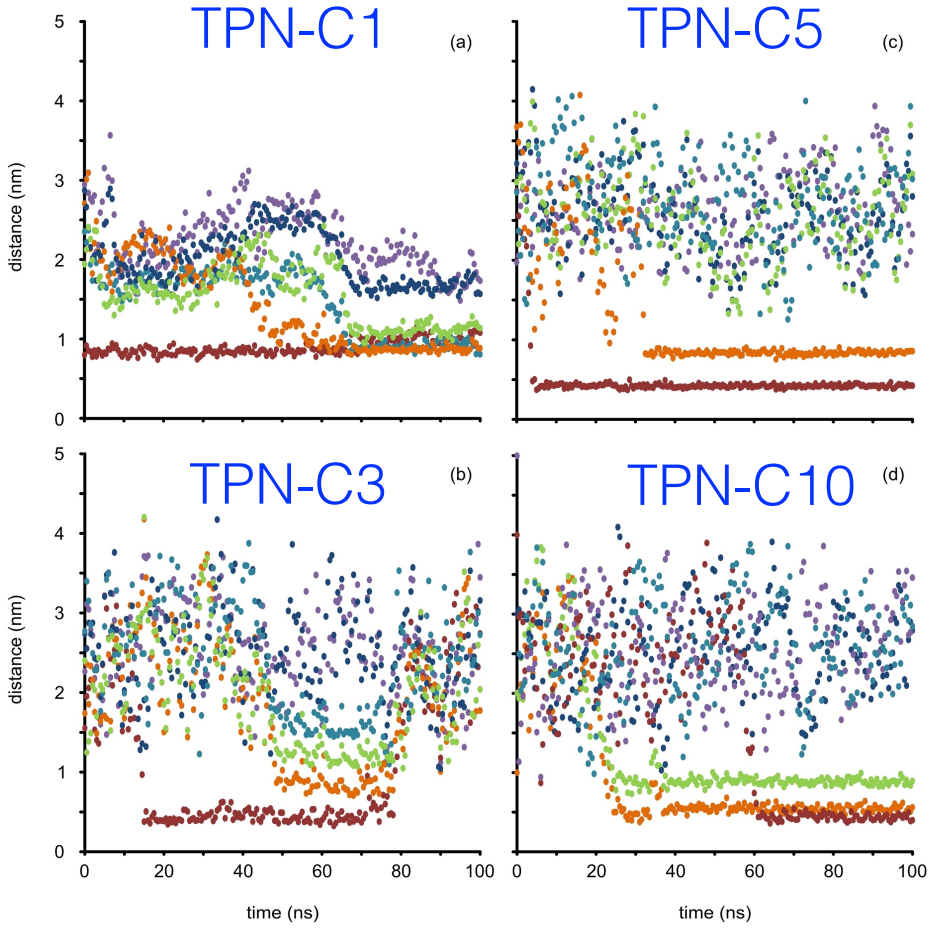


TPN-C0 stays dispersed
TPN-C1 aggregates
TPN-CN aggregates – not all the time
TPN-CNAcid aggregates

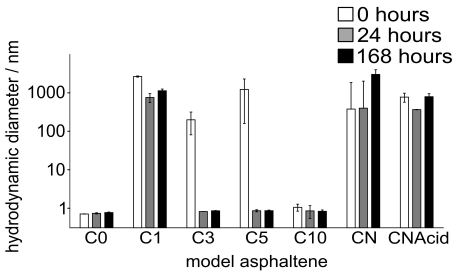


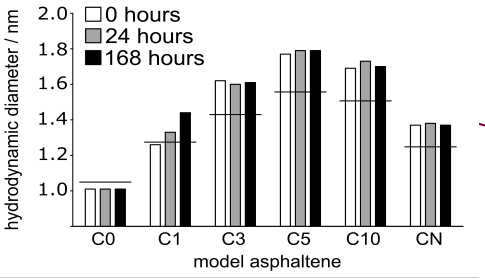
Molecular arrangement in the aggregate

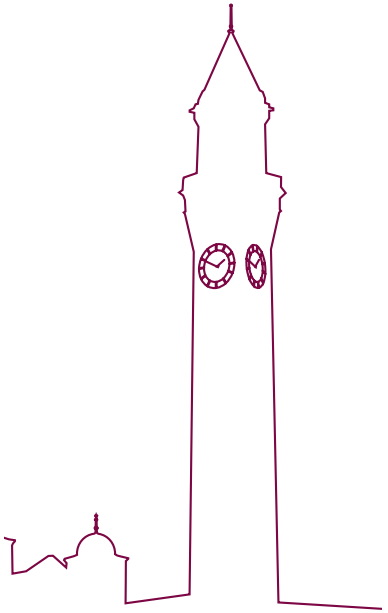
Calculated distances between the centers of mass (COM) for one molecule with the other six molecules, over 100 ns



TPN-C1 aggregates
TPN-C3 aggregates – several stacks
TPN-C5 aggregates – nanoscale
TPN-C10 aggregates – nanoscale

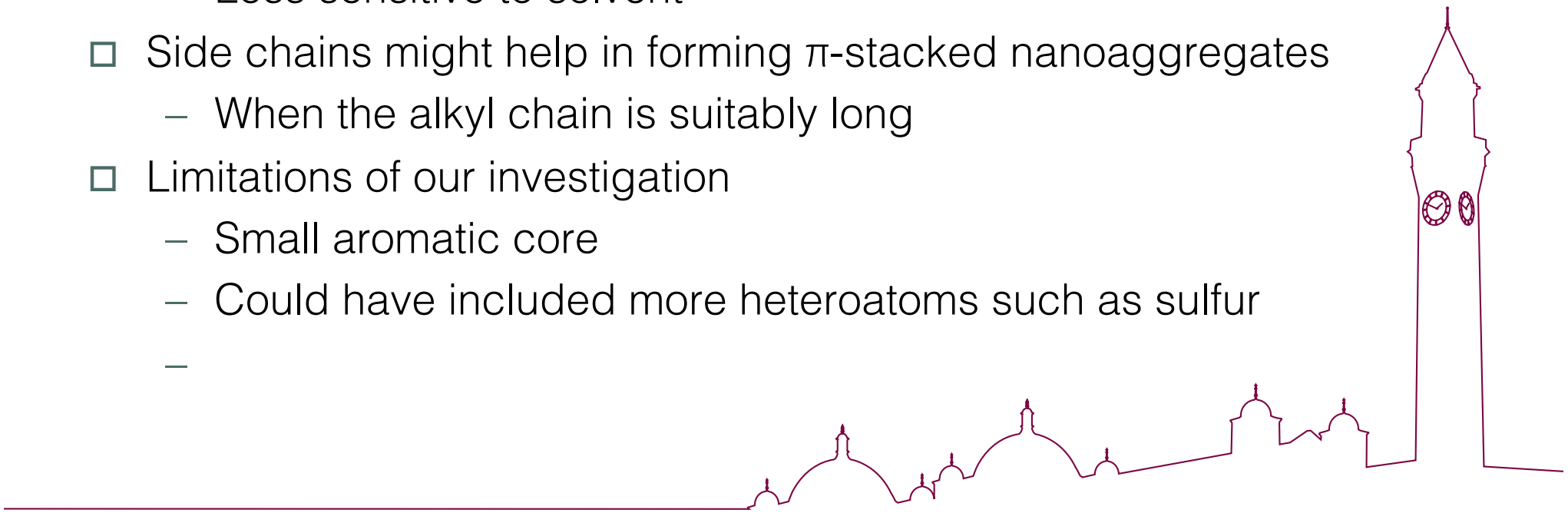






Summary

- Aggregation of PAH is determined by a balance of factors: π-π interactions, polar groups, steric hindrance, degree of solvation
- Molecular structure of PAH is key
- Polar groups, e.g. amide and acid, facilitate the formation of macroaggregates
  - Less sensitive to solvent
- Side chains might help in forming π-stacked nanoaggregates
  - When the alkyl chain is suitably long
- Limitations of our investigation
  - Small aromatic core
  - Could have included more heteroatoms such as sulfur
  -



Acknowledgement

Dorin

Joe

Greg

Jon

Rob

UNIVERSITY OF BIRMINGHAM

Thank you!

UNIVERSITY OF
BIRMINGHAM