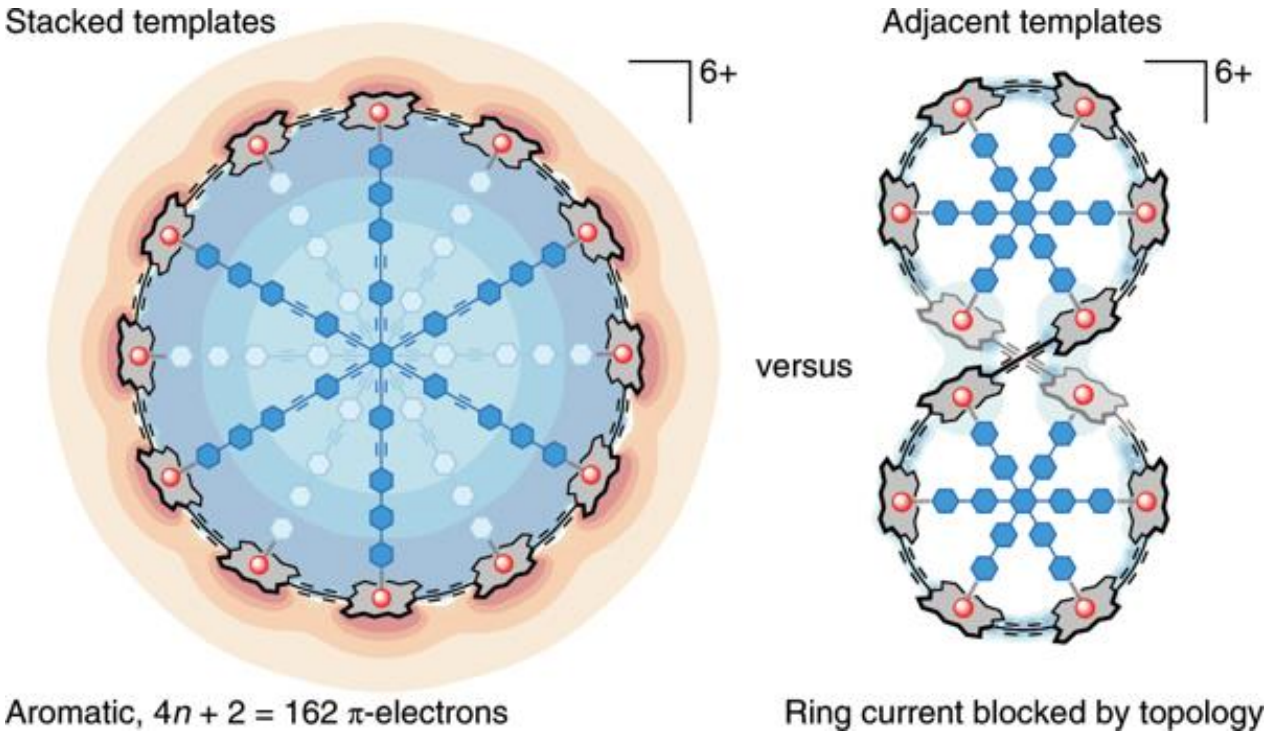
Global aromaticity at the nanoscale



Michel Rickhaus, Michael Jirasek, Lara Tejerina, Henrik Gotfredsen , Martin D. Peeks, Renée Haver, Hua-Wei Jiang, Timothy D. W. Claridge, Harry L. Anderson

Nature Chemistry **2020**, 12, 236–241

Published: January 20th

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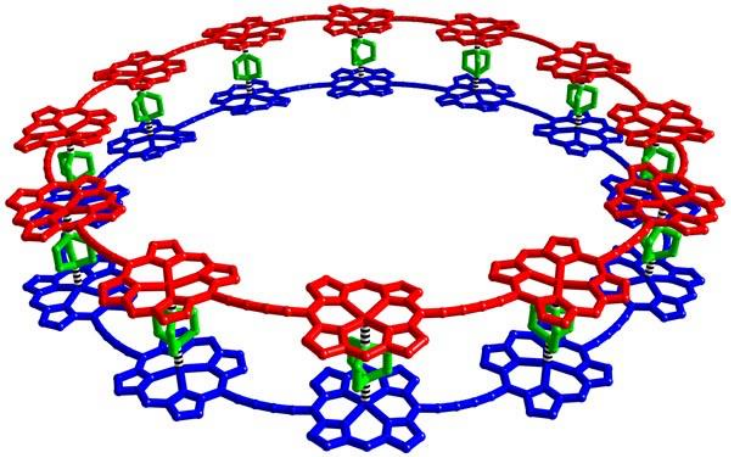
Harry Anderson: Professor at University of Oxford

Research areas:

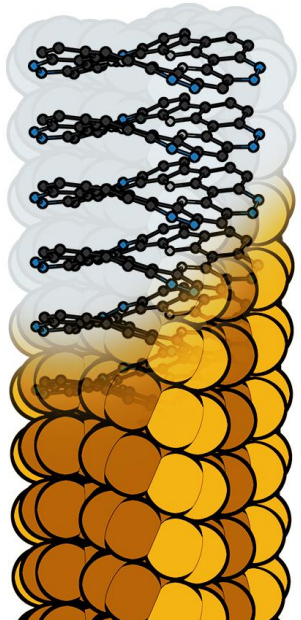
- π-Conjugated porphyrin nanostructures
- Switchable dyes for super-resolution microscopy
- Single-molecule electronic devices
- Polyyne rotaxanes, catenanes and cyclocarbons
- Understanding cooperativity and molecular recognition.



Michel Rickhaus: Group Leader at University of Zurich

Research area:

- Distorted polyaromatic molecules



http://research.chem.ox.ac.uk/harry-anderson.aspx
https://www.chem.uzh.ch/en/research/groups/rickhaus/research.html

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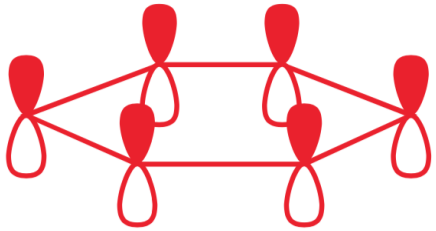
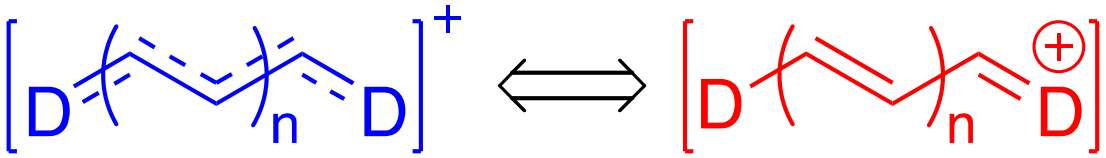
Criteria for aromaticity:

- Cyclic molecule, conjugated π–system
- Planar
- Follows Hückel-rule: 4n+2 π–electrons

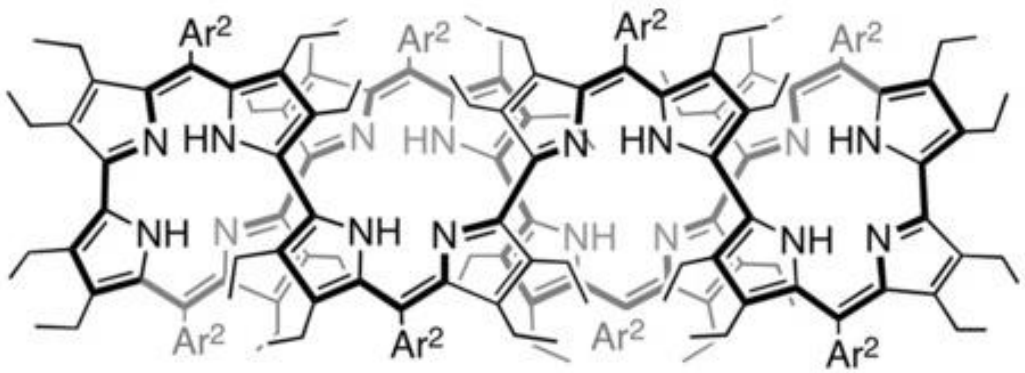


- Electron-delocalization is limited by symmetry-breaking transitions
- e.g. polymethine dyes: localized charge after exceeding critical chain length



R. Gieseking, M. Ravva, V. Coropceanu, J.-L. Brédas, *J. Phys. Chem. C* **2016**, 120, 9975-9984.

- Size limit of aromatic rings unknown
- Largest aromatic ring reported before: 62 π–electrons



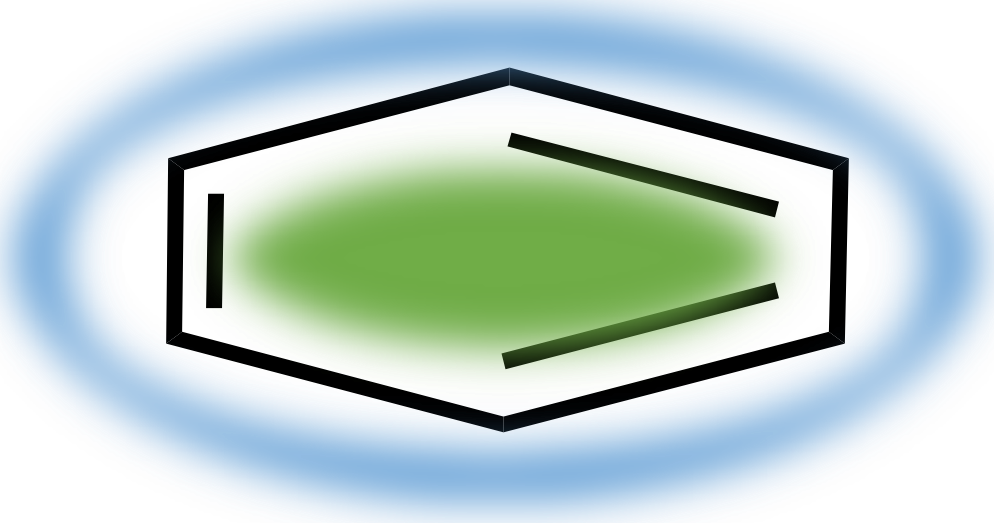
2 (64π)

T. Yoneda, T. Soya, S. Neya, A. Osuka, *Chem. Eur. J.* **2016**, *22*, 14518.

Clayden, J., Greeves, N. & Warren, S. *Organic Chemistry,* Oxford Univ. Press, Oxford, 2012.

Ring current and NMR shifts

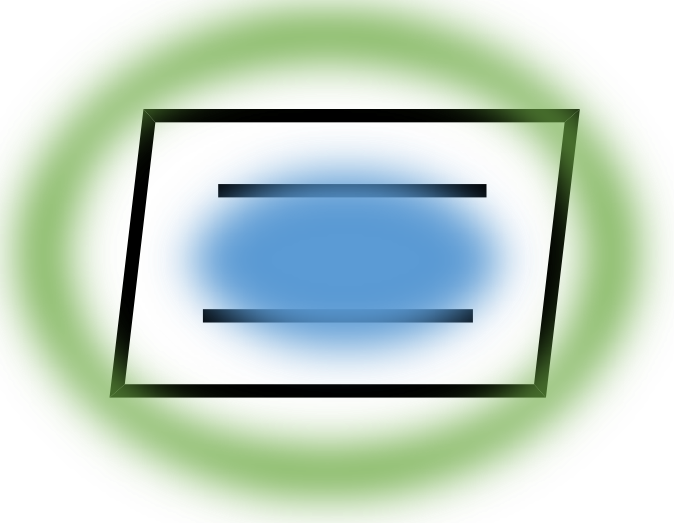
Aromatic compounds



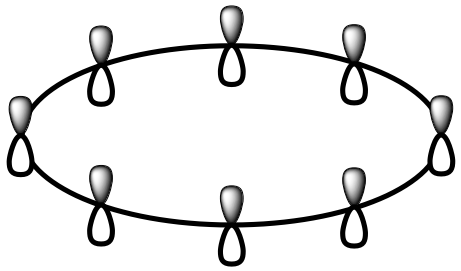
Downfield shift

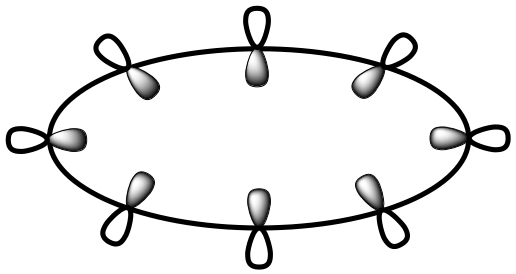
Upfield shift

Antiaromatic compounds



→ determination of aromatic character by NMR–spectroscopy





Annulenes: π–orbitals perpendicular to ring plane
Trannulenes: π–orbitals in plane

Both follow the Hückel rule

G. Burley, *Angew. Chem. Int. Ed.* **2005**, 44, 3176 –3178.

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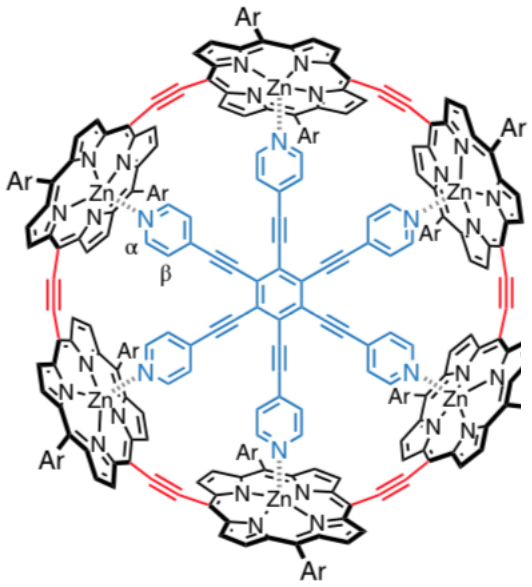
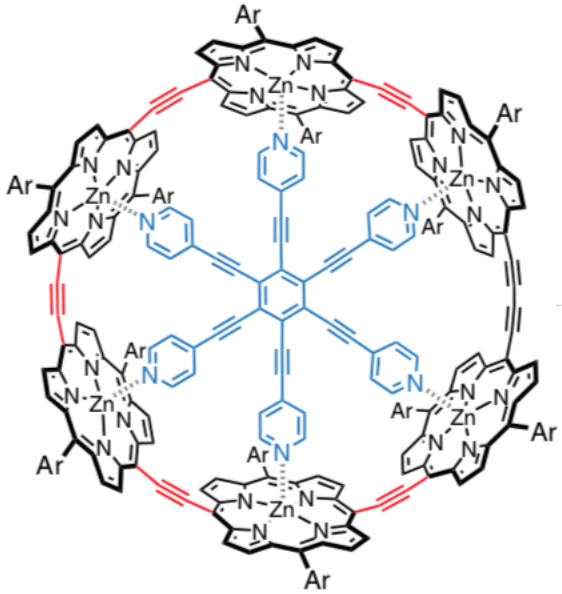
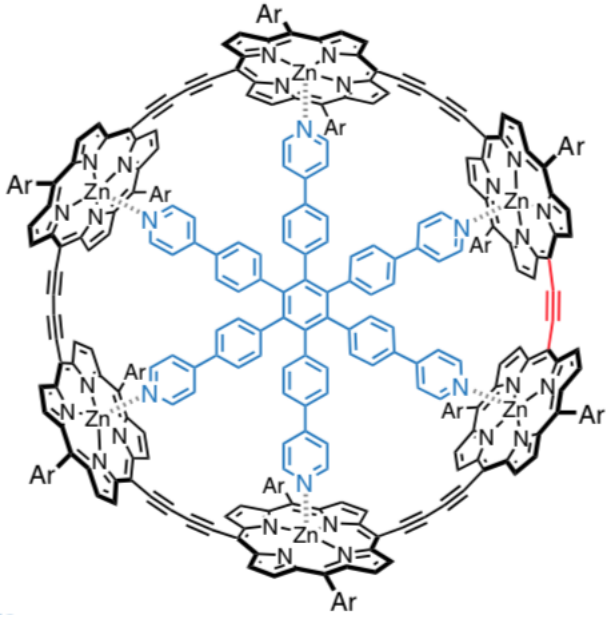
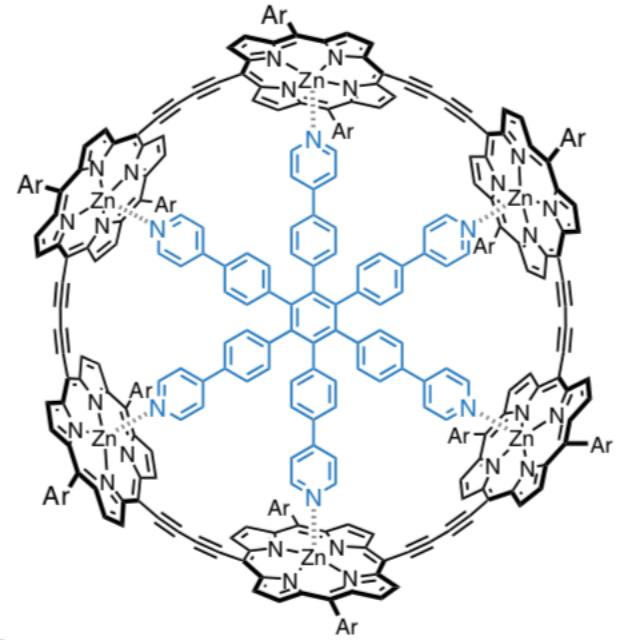
- Synthesis of porphyrin nanoring complexes
- Variation of number of π–electrons, largest complex: 162 π–eletrons
- Examination of 2+, 4+, and 6+ oxidation states









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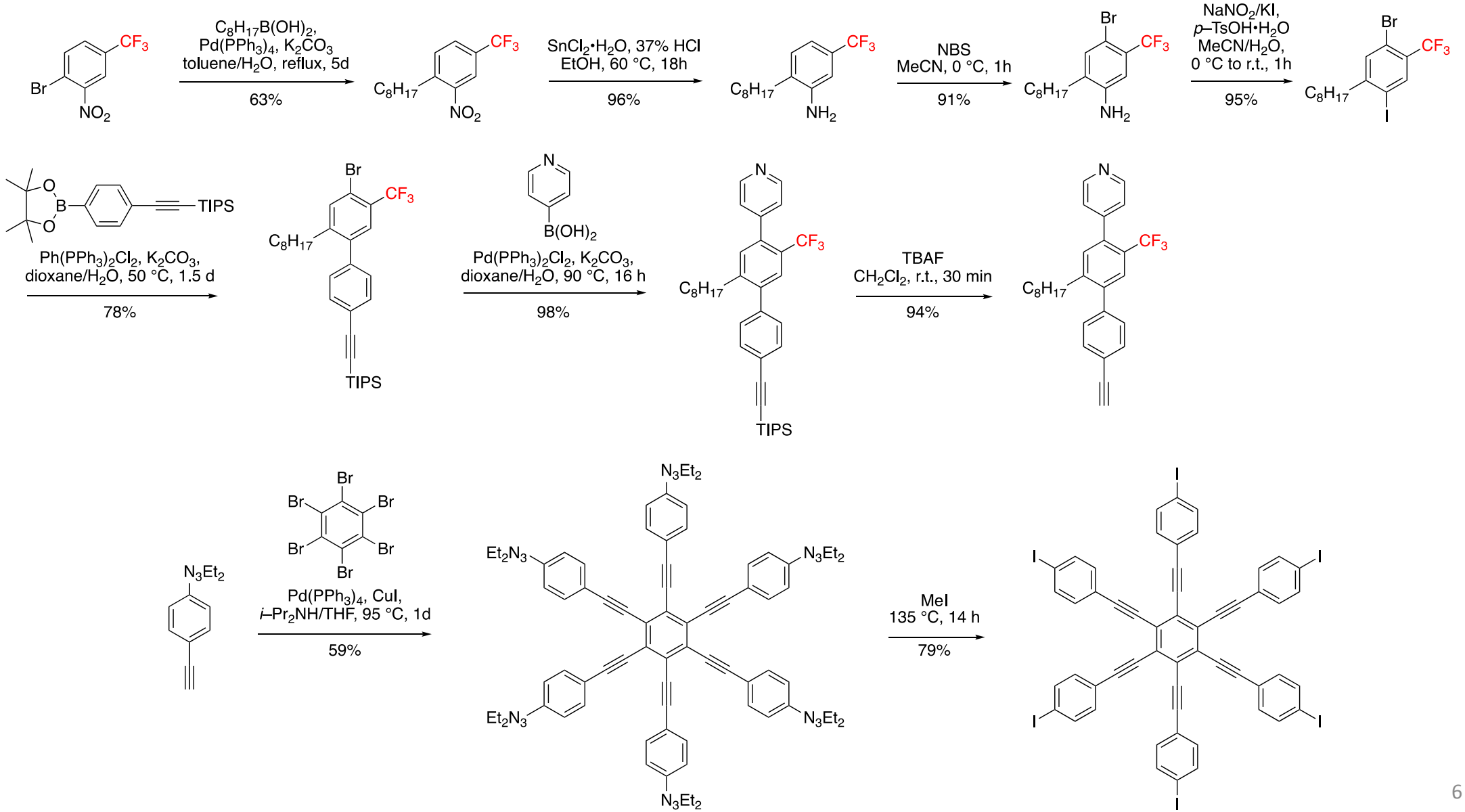
Example for template synthesis



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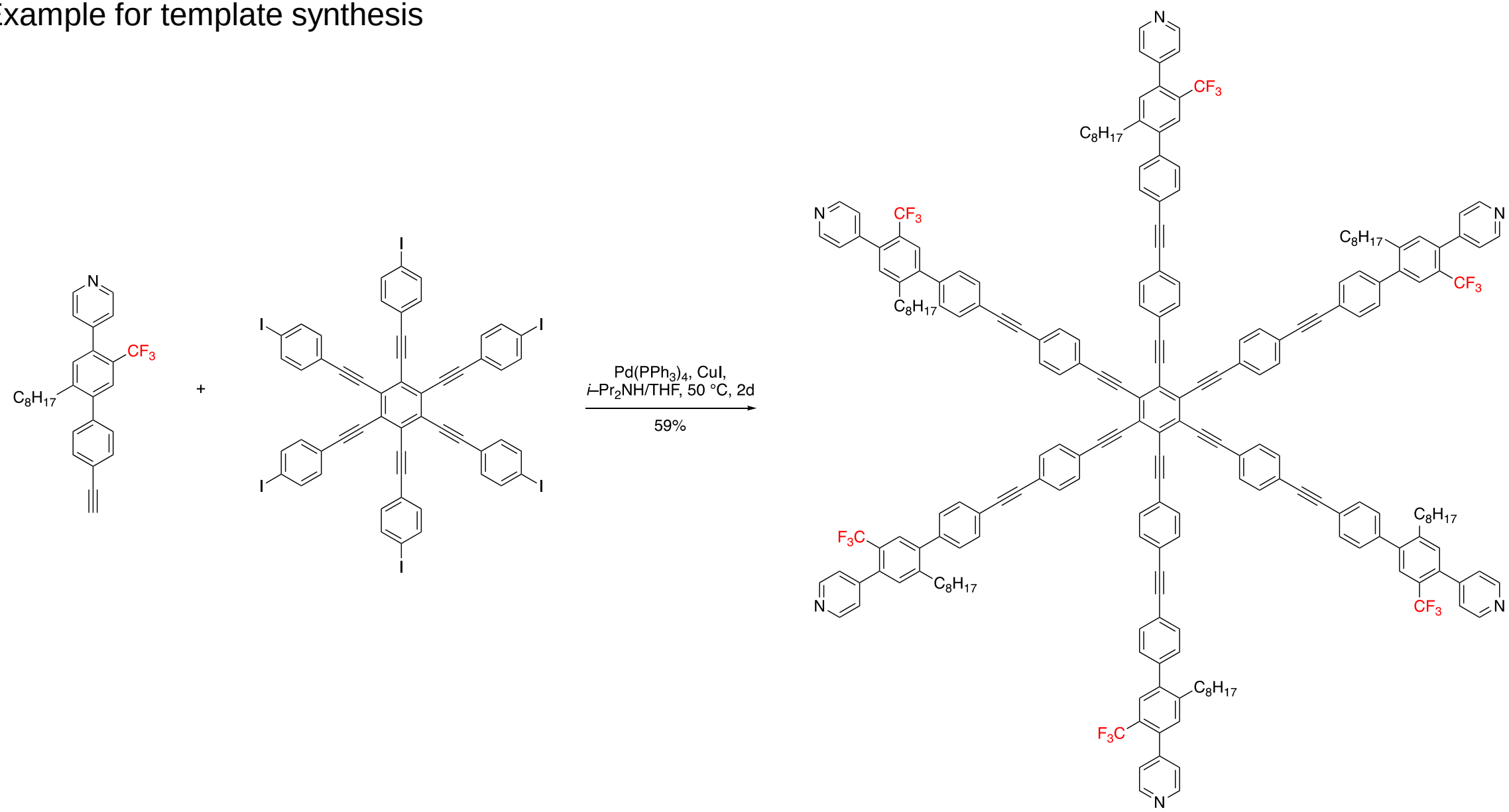
Example for template synthesis



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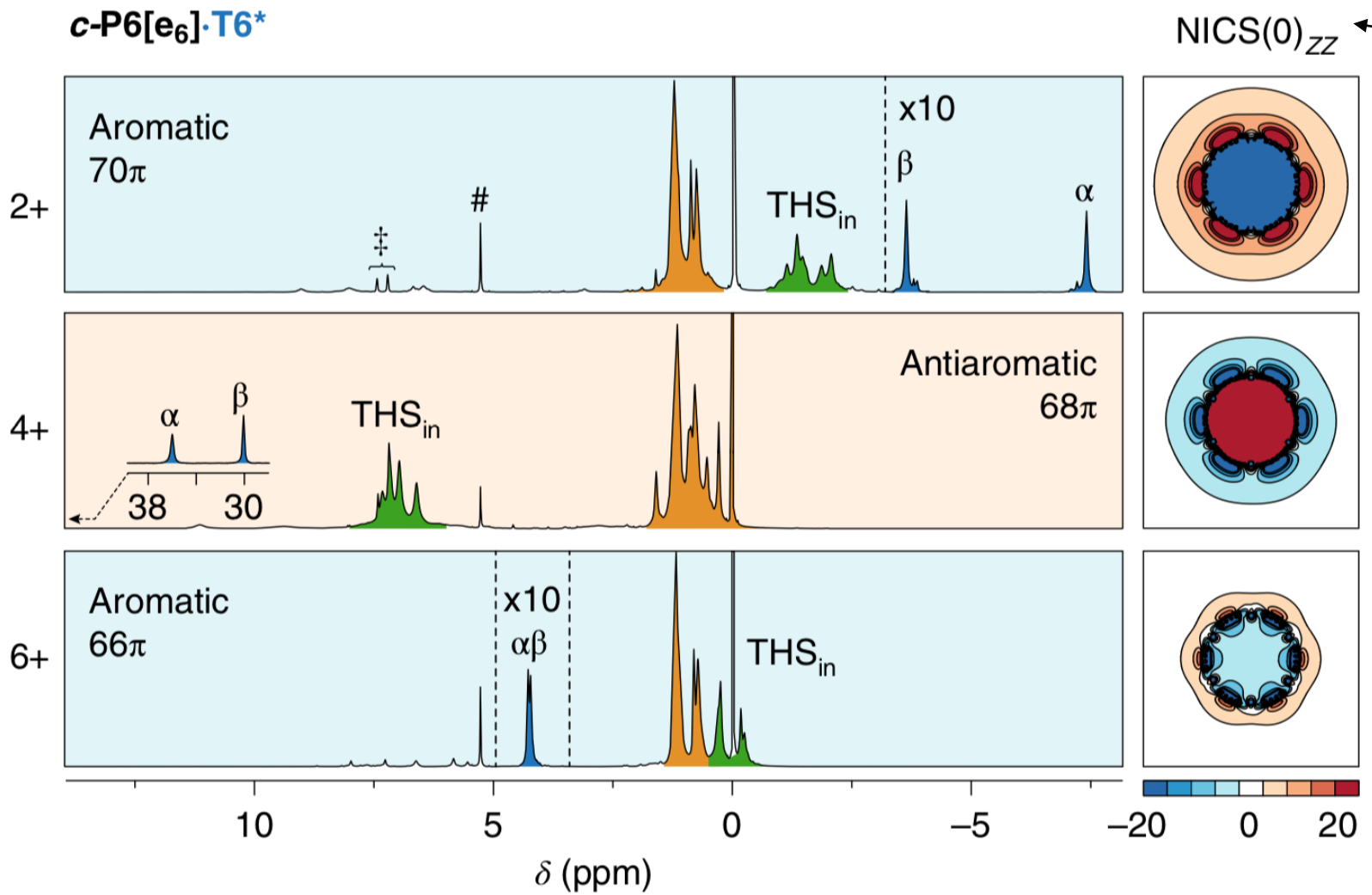
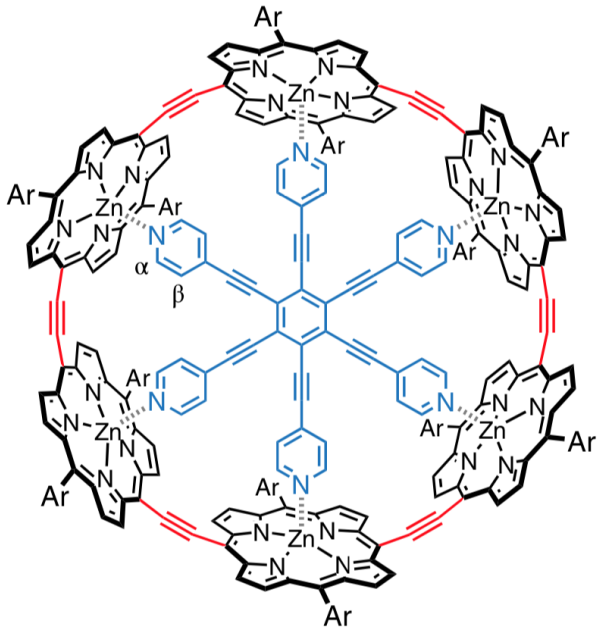


Nucleus-independent chemical shift (NICS) calculations: calculates magnetic shielding of ring center



- Interconversion of THS_{in} and THS_{out} is slow on the NMR timescale
- Neutral molecule: no ring current because local porphyring ring current dominates

→ Mixed valence state is essential for nanoscale charge delocalization

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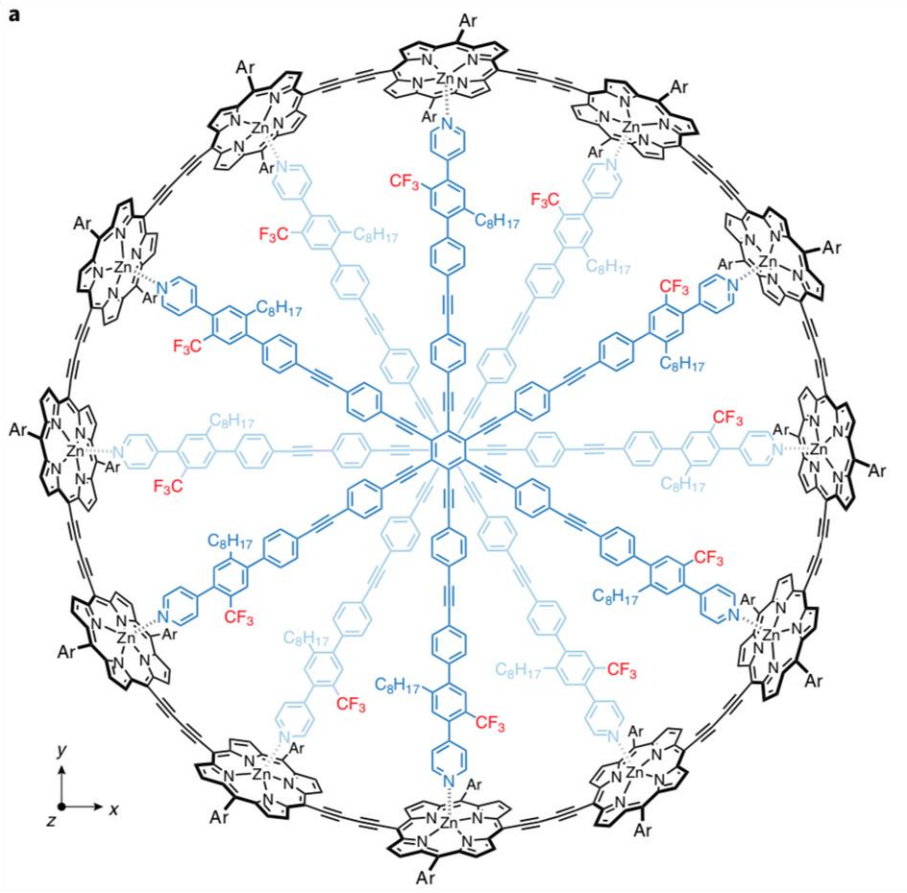
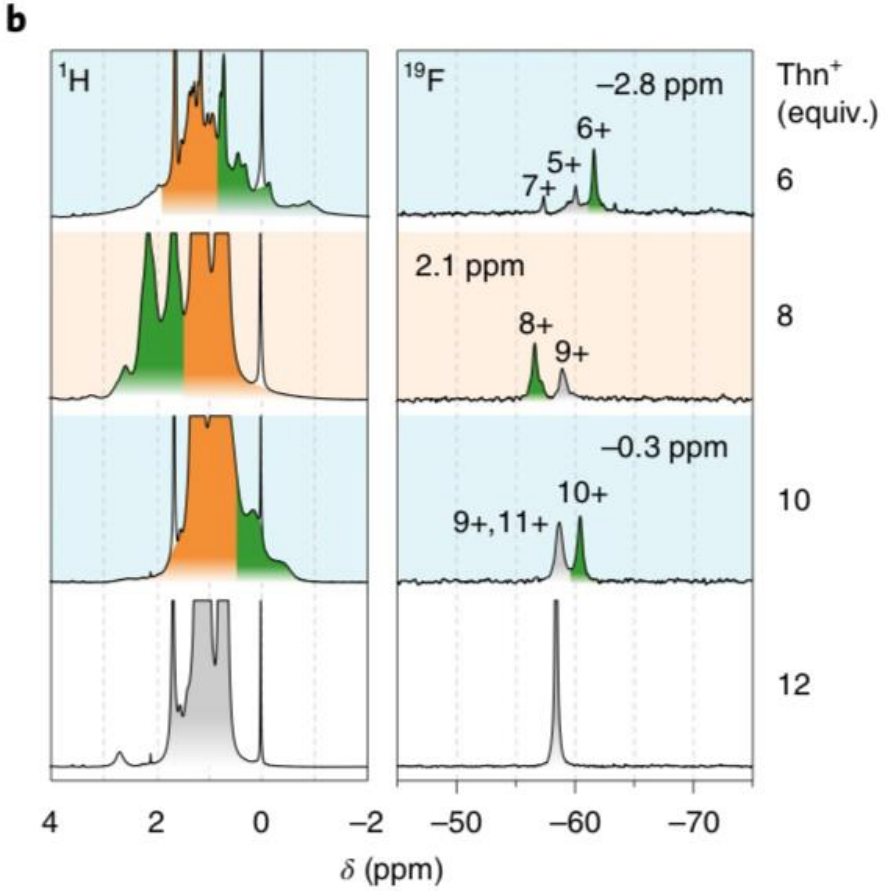
Examination of influence of topology on aromaticity





- Change in shifts of THS_{in} in ^{1}H NMR
- Change in shifts of CF_3 in ^{19}F NMR

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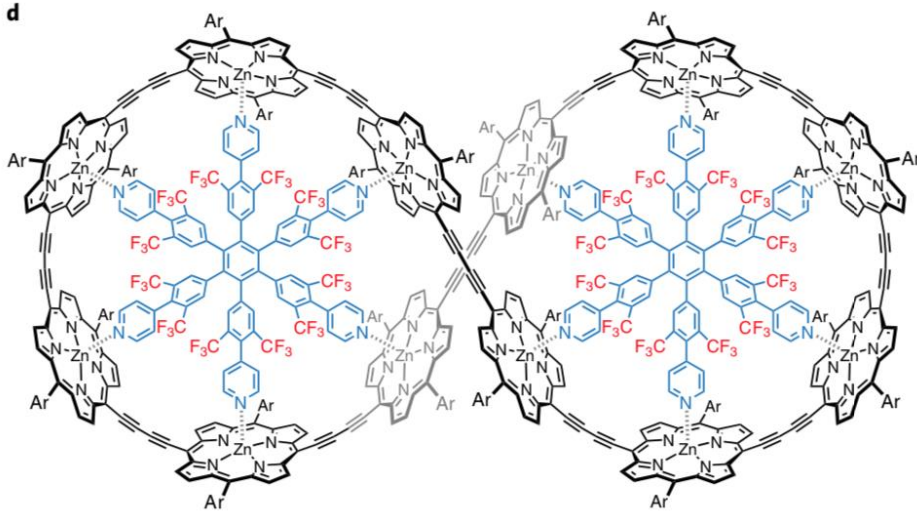
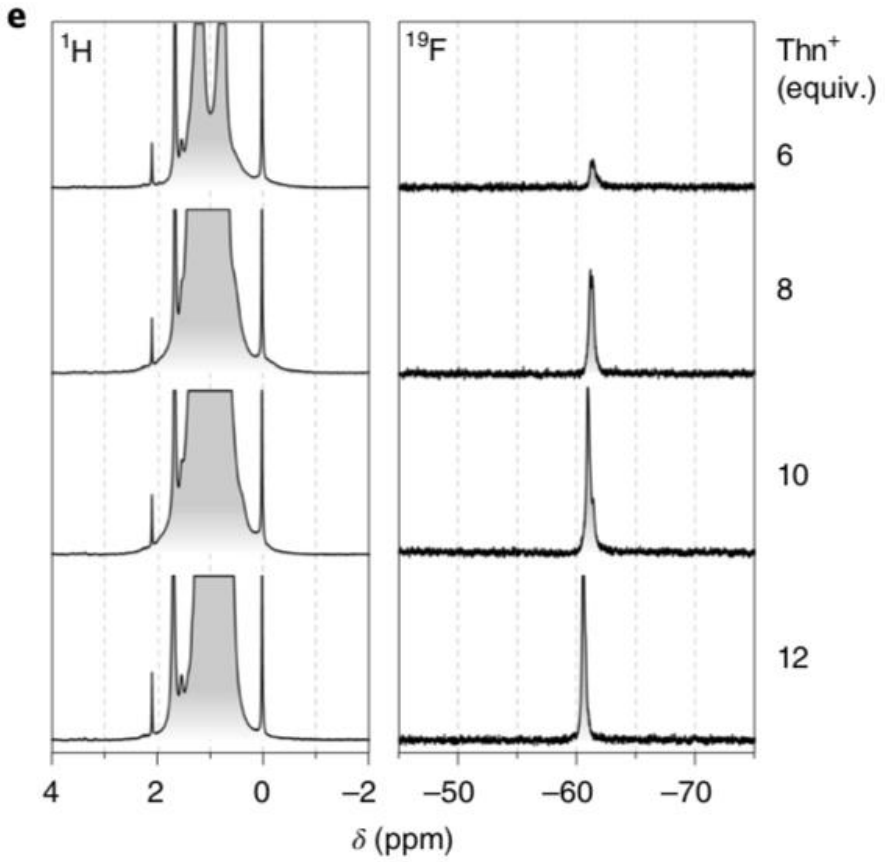
Examination of influence of topology on aromaticity





No change in shifts in ^{1}H and ^{19}F NMR

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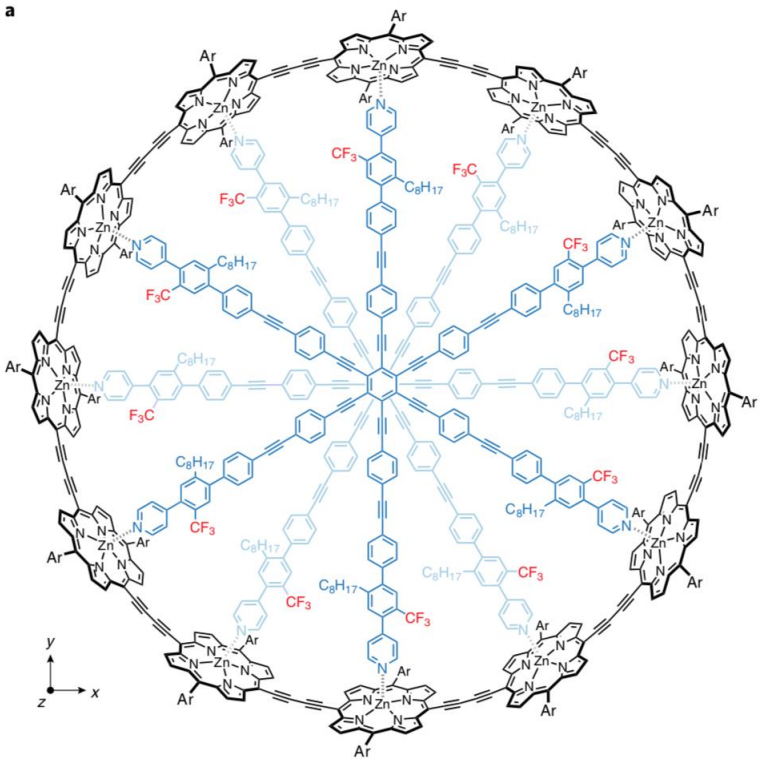
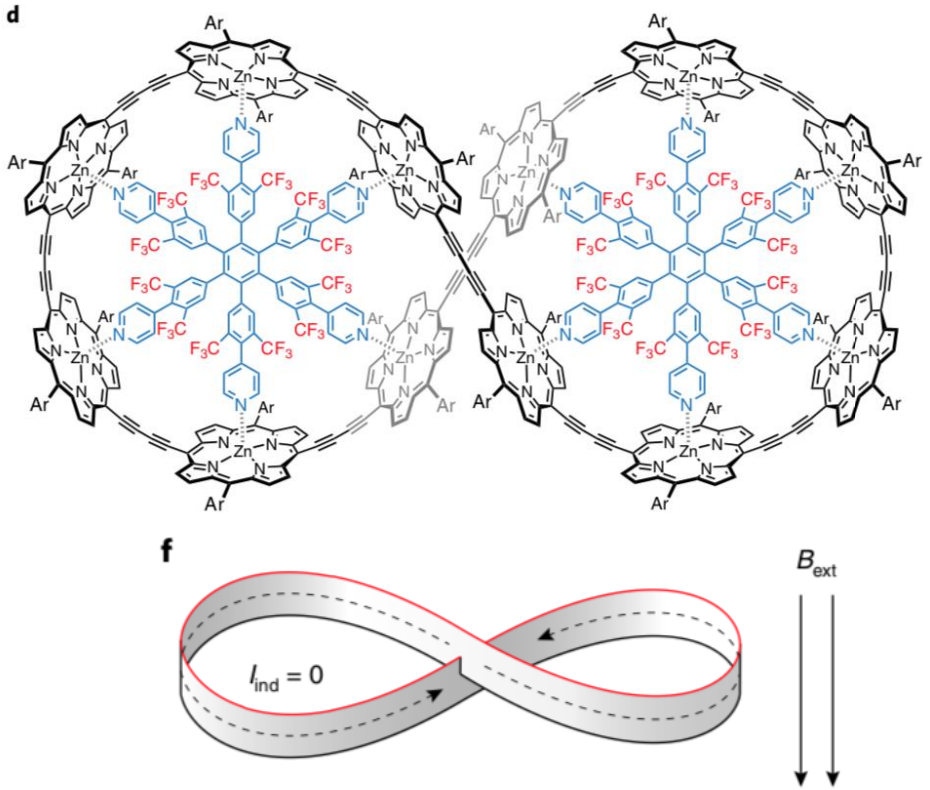
Examination of influence of topology on aromaticity



Exhibits ring current



Does not exhibit ring current
Opposite currents of ring loops cancel → no ring current

Conclusion

- Report of largest aromatic ring with 162 π–electrons
- Hückel‘s rule can be applied to trannulenes as well
- Hückel‘s rule is still valid for large systems
- Mixed valence state is necessary for charge delocalization
- Aromaticity can be controlled by geometry