The Pseudo-π method and the current densities of porphyrinoid nanostructures.

By

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INTRODUCTION

- Photoelectronics and other application fields
- Appealing topology
- Synthesis of porphyrinoid macrorings has been reported recently
- Aromatic in character
- All 26 π electrons conribute to the conjugation
- Coordination complex of Zn and free-base porphyrin.
- We decided to study the current densities in the Zn-based porphyrinoid nanostructures.

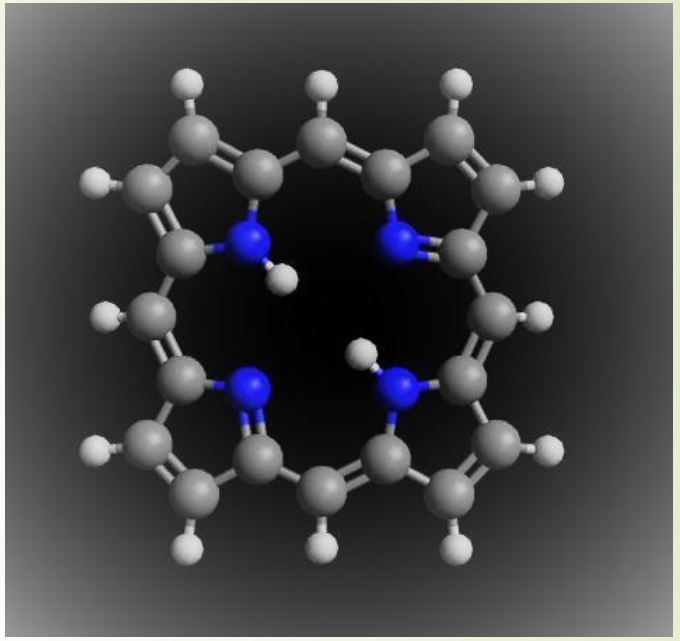


Figure 1. Free-base Porphyrin

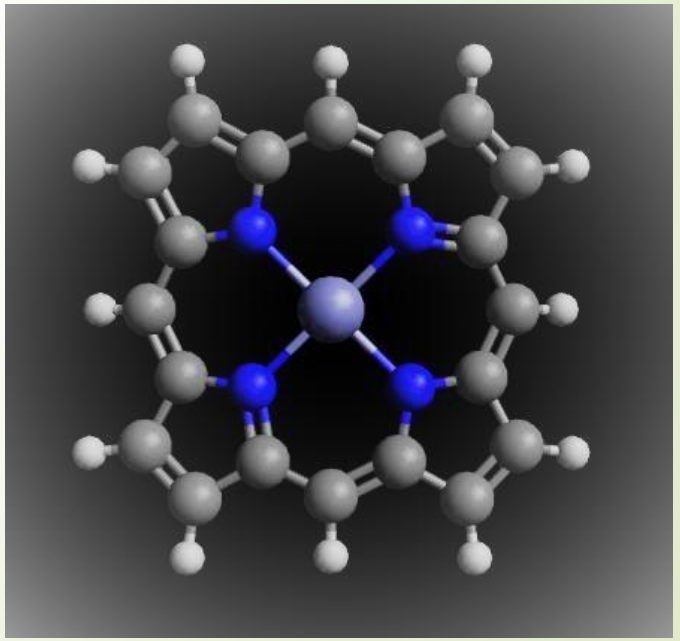


Figure 2. Zn-base porphyrin

MAIN TOPICS

1. *Magnetically Induced Current Densities in Zinc Porphyrin Nanoshells. (5 Molecules)*

   A. Mahmood, M. Dimitrova, L.N. Wirz and D. Sundholm, Magnetically Induced Current Densities in Zinc Porphyrin Nanoshells, *J. Phys. Chem. A*, **2022**, 126, 1936-1945.

2. *Magnetically Induced Current Densities in π-Conjugated Porphyrin Nanoballs. (7 Molecules)*

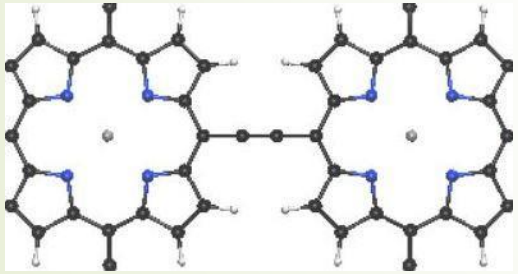
   A. Mahmood, M. Dimitrova, L.N. Wirz and D. Sundholm, Magnetically Induced Current Densities in π-Conjugated Porphyrin Nanoballs, *J. Phys. Chem. A*, **2022**, 126, 7864-7873.

3. Current density calculations of Zn-porphyrin$_{40}$ Nanorings. (2 Molecules)

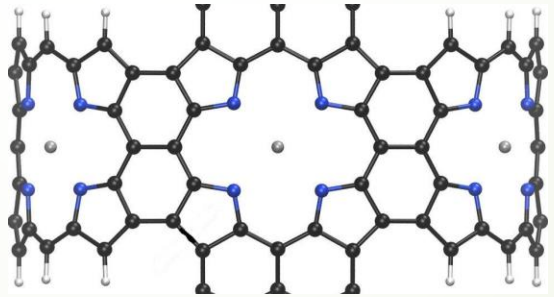
   A. Mahmood, M. Dimitrova, D. Sundholm, Current-Densities Calculations on Zn-Porphyrin$_{40}$ Nanorings, *J. Phys. Chem. A.* **2023**, *127*, 7452-7459.

MOLECULAR STRUCTURE

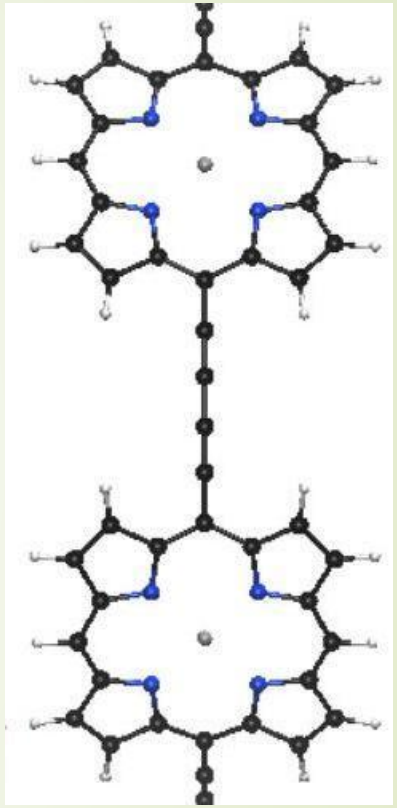
- Constructing small polyhedral graphs whose vertices had degree-4.
- polyhedral vertices ↔ Zn−porphyrin units
- Their edges ↔ ethyne bridges
  butadiyne bridges
  fusing neighboring Zn−porphyrin units.



(a)



(b)



(c)

Figure 3. Three differences bridges (a) Ethyne linker, (b) Fused neighbors and (c) Butadiyne linker used in our study

1. J. Cremers, S. Richert, D. V. Kondratuk, T. D. W. Claridge, C. R. Timmel, H. L. Anderson, *Chem. Sci.* **2016**, 7, 6961−6968.
2. J. Cremers, R. Haver, M. Rickhaus, J. Q. Gong, L. Favereau, M. D. Peeks, T.D.W. Claridge, L. M. Herz, H. L. Anderson, *J. Am. Chem. Soc.* **2018**, 140, 5352−5355.

COMPUTATIONAL METHODS

- Structures optimized at the B3-LYP/D3(BJ)/def2-SVP level
- Nuclear magnetic resonance (NMR) shielding tensors at the same level
- Calculated magnetically induced current densities (MICD) with GIMIC
- The ParaView program for MICDs visualization
- The MICD strengths were integrated numerically
- The MICD strengths determine the degree of aromaticity

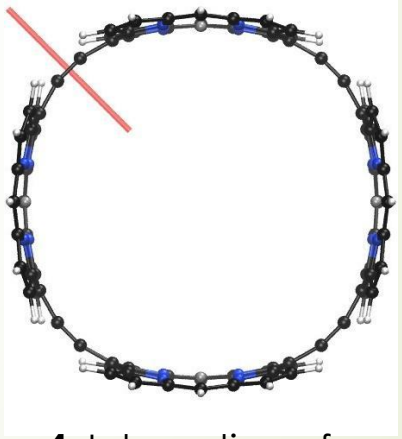


Figure 4. Integration of current flux through a plane for the global ring current

NANOSHELLS

- **Molecule 1:**
  - an ethyne-bridge
  - Nanotube with sealed ends
- **Molecule 2:**
  - an ethyne-bridge
  - Nanotube with open ends
- **Molecule 3:**
  - Clam-like porphyrinoid
  - fused Zn−porphyrins & butadiyne bridges linkers
- **Molecule 4:**
  - fused Zn−porphyrins.
  - Perpendicular cross-belt

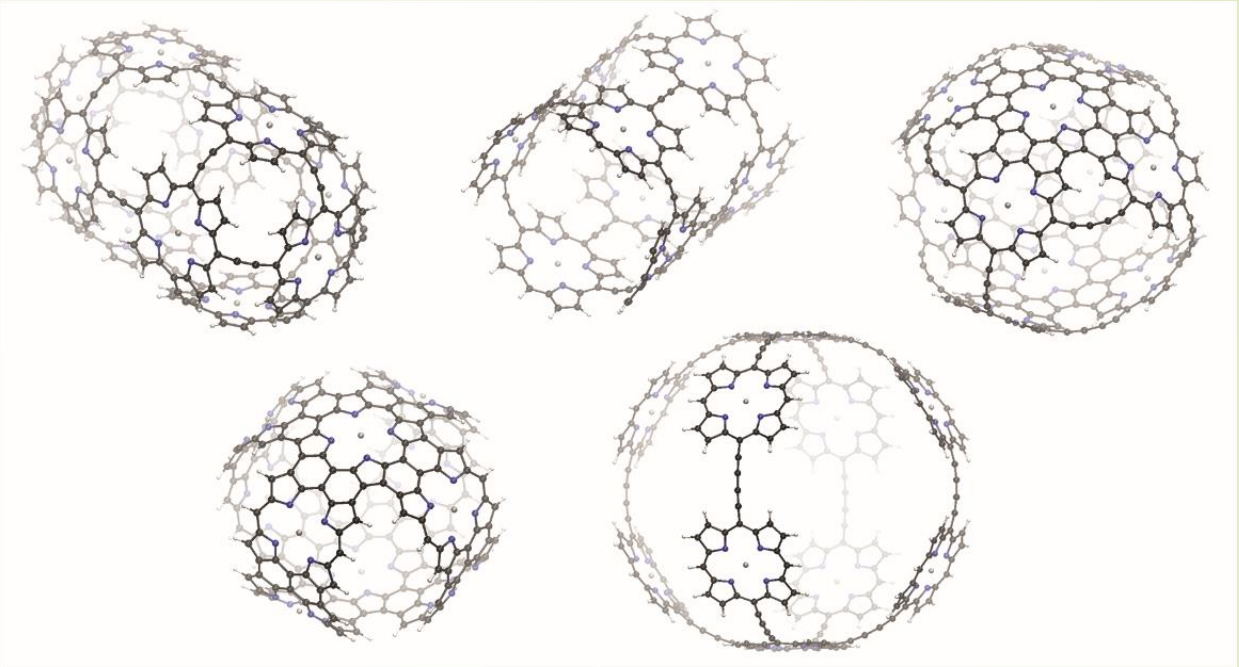


Figure 5. Structural representation of five distinct molecules

- **Molecule 5:**
  - Butadiyne bridges
  - Perpendicular cross-belt
  - Recently synthesized molecule

1. J. Cremers, S. Richert, D. V. Kondratuk, T. D. W. Claridge, C. R. Timmel, H. L. Anderson, *Chem. Sci.* **2016**, 7, 6961−6968.
2. J. Cremers, R. Haver, M. Rickhaus, J. Q. Gong, L. Favereau, M. D. Peeks, T.D.W. Claridge, L. M. Herz, H. L. Anderson, *J. Am. Chem. Soc.* **2018**, 140, 5352−5355.

- Molecule 1 (with sealed ends) & Molecule 2 (with open ends) are anti-aromatic sustaining paratropic ring currents
- The ring current strength of Molecule-1 is -26.2 nA/T
- For Molecule-2 it is -17.9 nA/T.

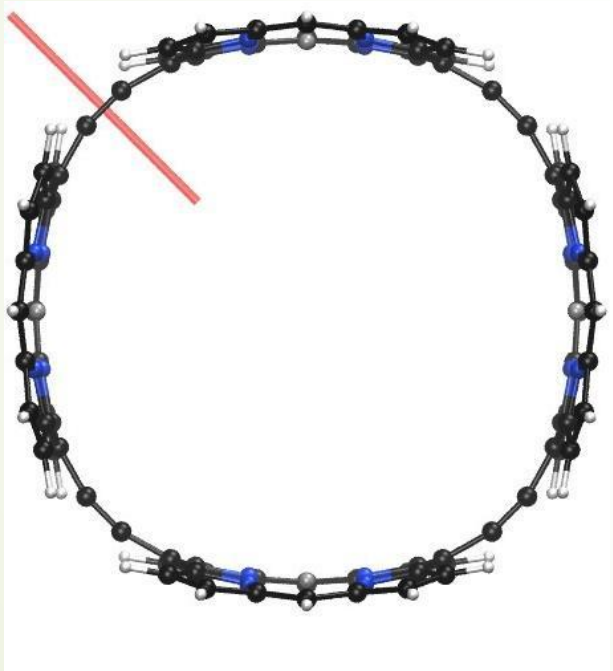


Figure 6. Red bars illustrating integration planes in molecule 2 used in the current density analysis

Figure 7. Illustration of global paratropic ring current in the Molecule 2.

The fused porphyrinoids (molecule 3 and 4) have complicated current-density pathways that differ from the ones usually appearing in porphyrinoids.

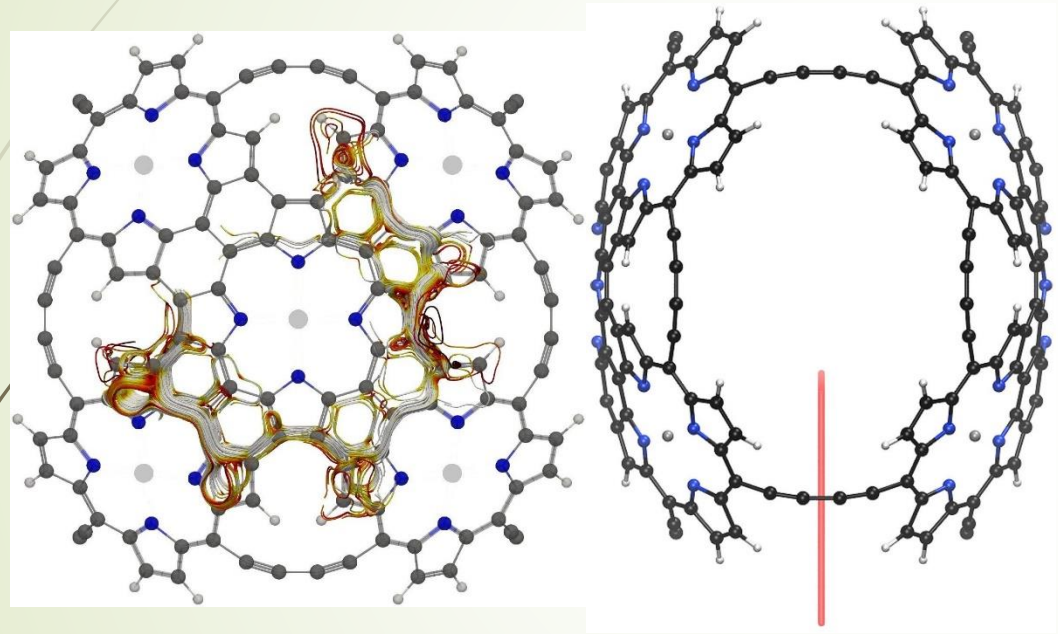


Figure 8. Current density pathways in Molecule 3.

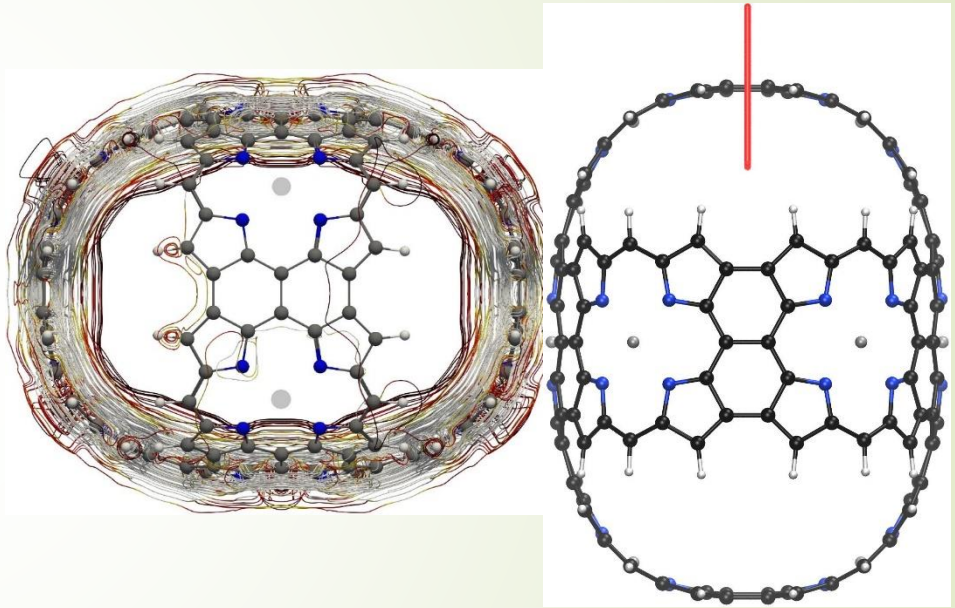


Figure 9. Current density pathways in Molecule 4.

- The neutral molecule 4 is antiaromatic
- The aromatic character of molecules 4 changes upon oxidation
- The dication is nonaromatic

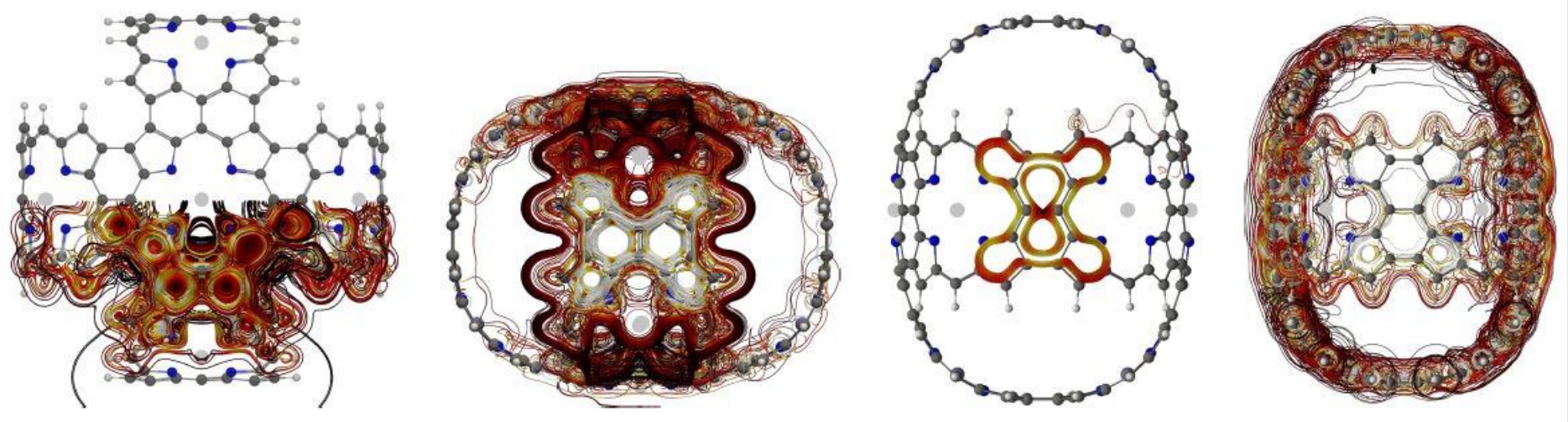


Figure 10. Current density pathways in the dication of Molecule-4 The global ring current is -0.9 nA/T

- The neutral molecule 5 is nonaromatic
- Molecule 5 is locally aromatic sustaining ring currents in the individual porphyrin units
- Oxidation of 5 leads to global aromaticity
- The current strength of 34.6 nA/T

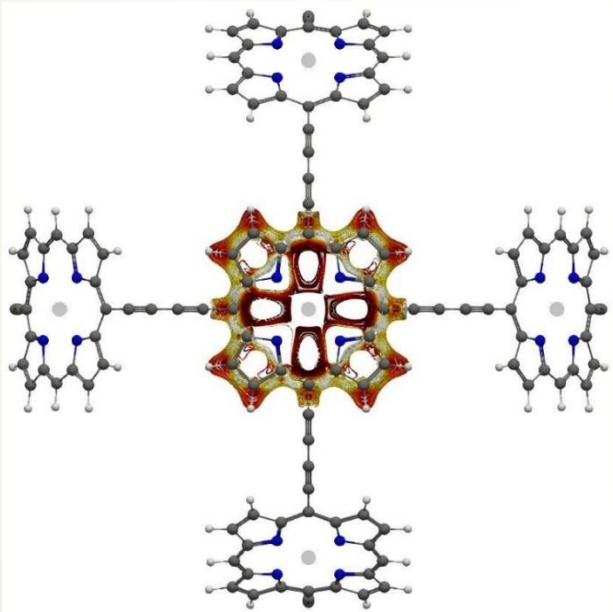


Figure 11. Local aromatic current pathways in Molecule 5.

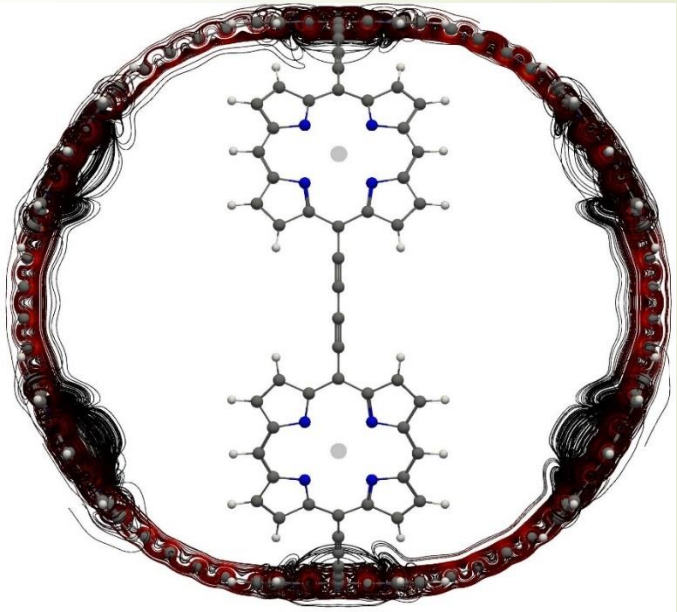


Figure 12. Global aromaticity in dication of Molecule 5.

1. J. Cremers, S. Richert, D. V. Kondratuk, T. D. W. Claridge, C. R. Timmel, H. L. Anderson, *Chem. Sci.* **2016**, 7, 6961−6968.
2. J. Cremers, R. Haver, M. Rickhaus, J. Q. Gong, L. Favereau, M. D. Peeks, T.D.W. Claridge, L. M. Herz, H. L. Anderson, *J. Am. Chem. Soc.* **2018**, 140, 5352−5355.

NANOSHELLS CURRENT STRENGTHS

Table 1. Strength of the Diatropic and Paratropic Contributions to the Net Strength of the Current Density (in $nA \cdot T^{-1}$) passing the integration planes of molecules.

Molecules	Diatropic	Paratropic	Net
Molecule-1	1.2	-27.4	-26.2
Molecule-2	2.8	-20.7	-17.9
Molecule-3	6.8	-8.6	-1.8
Molecule-4	5.2	-218.0	-212.8
Molecule-4(Dication)	19.5	-20.4	-0.9
Molecule-5	6.4	-8.9	-2.4
Molecule-5(Dication)	34.7	-0.1	34.6

PORPHYRIN CROSS-BELTS

1. **Molecule 1:** b-P10·T6·$(T2)^2$
2. **Molecule 2:** b-P12·T6·$(T3)^2$
3. **Molecule 3:** b-P14·T6·$(T4)^2$
4. **Molecule 4:** b-P14·T8·$(T3)^2$
5. **Molecule 5:** b-P16·T8·$(T4)^2$
6. **Molecule 6:** b-P18·T10·$(T4)^2$

- Neutral molecules were non-aromatic.
- The oxidation state of 1,3,4 and 6 were globally aromatic.

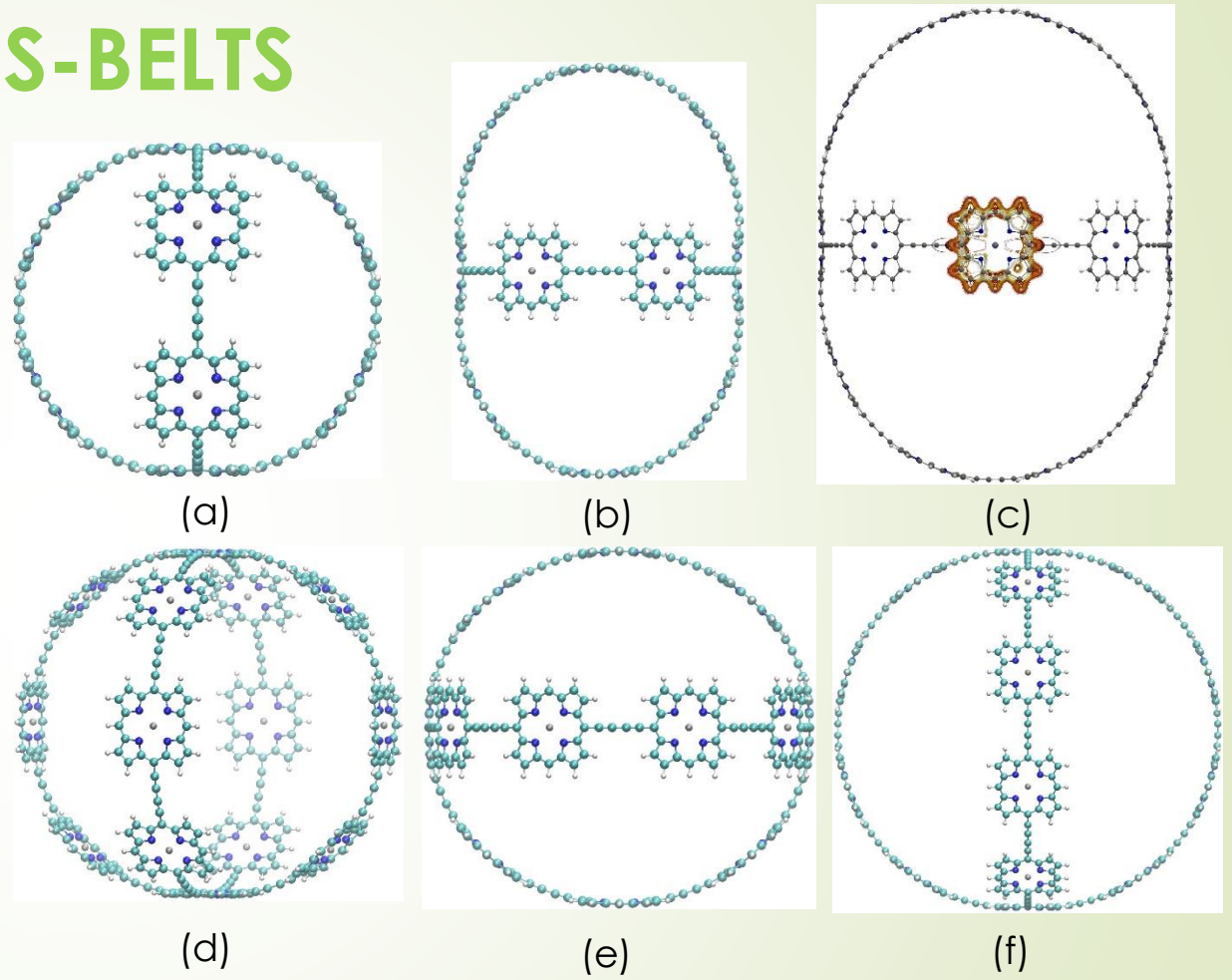
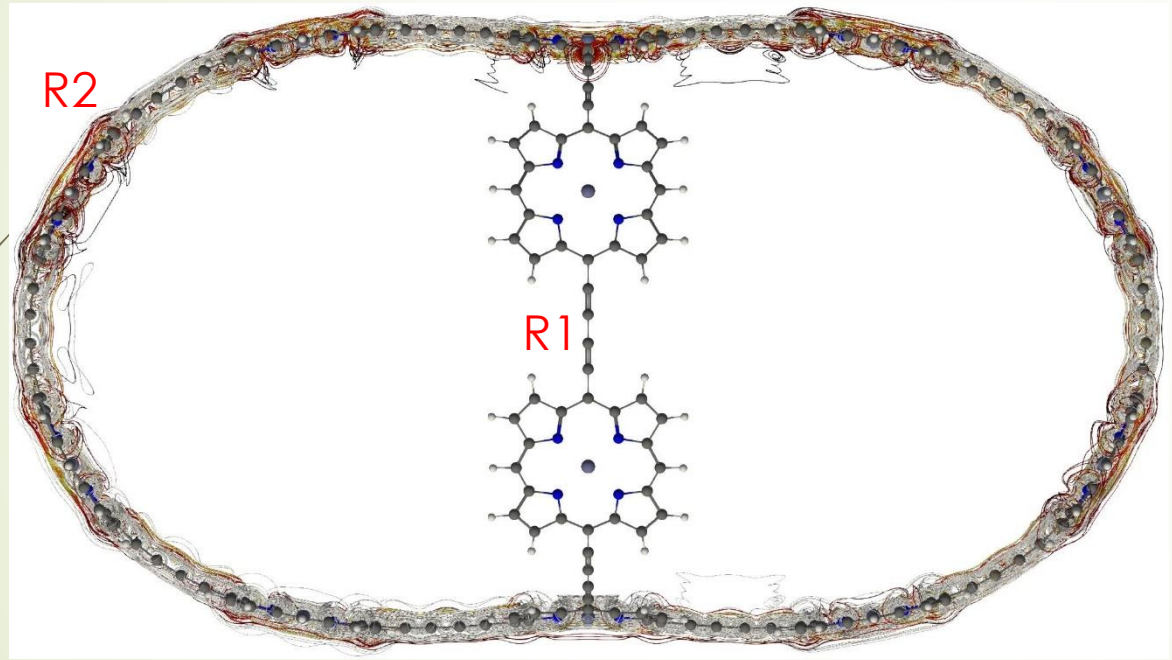


Figure 13. Structures of the six cross-belts molecules are depicted in (a) M1, (b) M2, (c) M3, (d)M4, (e)M5 and (f)M6 respectively

1. J. Cremers, S. Richert, D. V. Kondratuk, T. D. W. Claridge, C. R. Timmel, H. L. Anderson, *Chem. Sci.* **2016**, 7, 6961–6968.
2. J. Cremers, R. Haver, M. Rickhaus, J. Q. Gong, L. Favereau, M. D. Peeks, T.D.W. Claridge, L. M. Herz, H. L. Anderson, *J. Am. Chem. Soc.* **2018**, 140, 5352–5355.

MOLECULE 3 b-P14·T6·$(T4)^2$

- Ring 1 (R1) has 6 Porphyrin units
- Ring 2 (R2) has 8 Porphyrin units
- Individual porphyrin rings are aromatic
- Dication is globally aromatic.



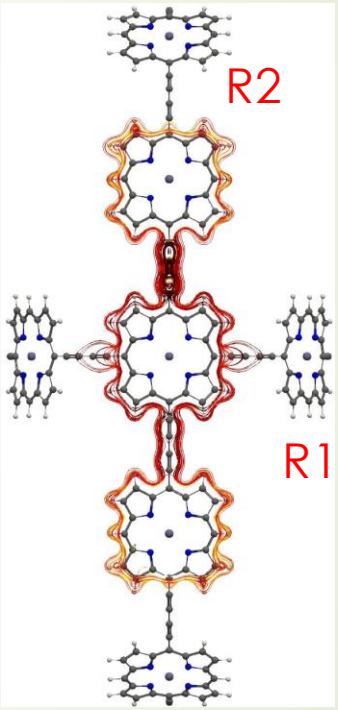
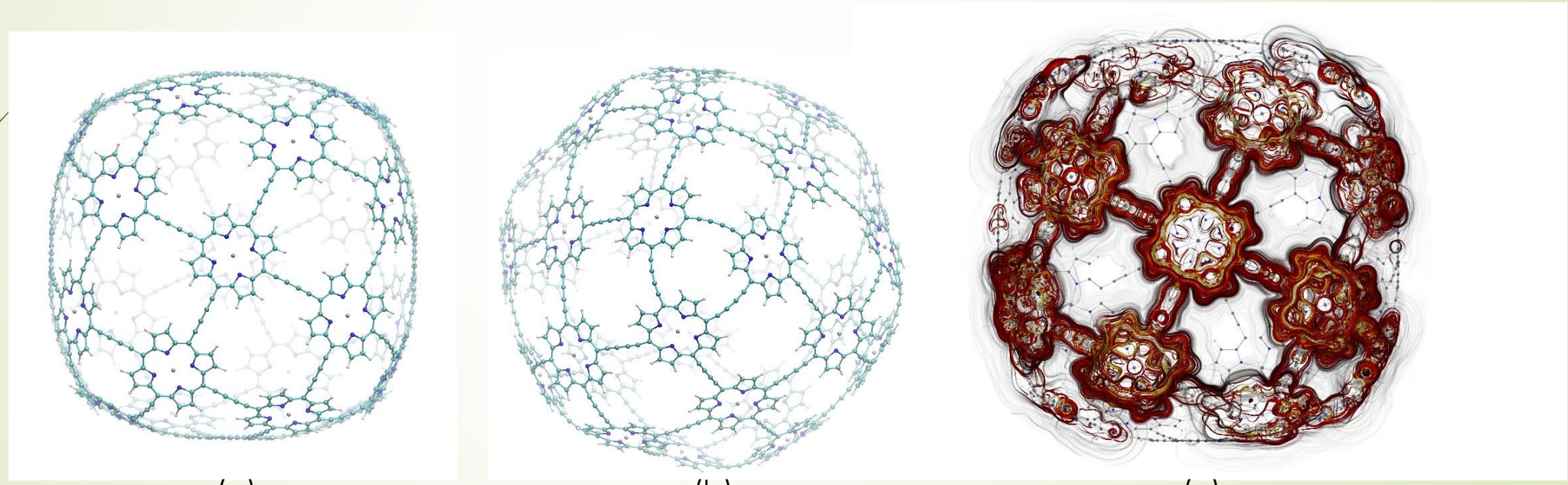


Figure 14. Current flow through dication of molecule 3

1. J. Cremers, S. Richert, D. V. Kondratuk, T. D. W. Claridge, C. R. Timmel, H. L. Anderson, *Chem. Sci.* **2016**, 7, 6961–6968.
2. J. Cremers, R. Haver, M. Rickhaus, J. Q. Gong, L. Favereau, M. D. Peeks, T.D.W. Claridge, L. M. Herz, H. L. Anderson, *J. Am. Chem. Soc.* **2018**, 140, 5352–5355.

PORPHYRIN NANOBALL b-P30

- **Molecule 7:** Nanoball
- It has 30 Porphyrin units
- Point group O (Octahedral)
- Global current is non-existent because of high symmetry
- It only has local and semi local ring currents



(a) (b) (c)

Figure 15. Nanoball structure and streamlines of the current pathway

RING CURRENTS IN ZN-PORPHYRIN NANOWHEELS

- A 40 Zn-porphyrin unit based macrocycle.
- **Nanowheel 1:** 40 units connected through the butadiyne linker.
- **Nanowheel 2:** 40 units (Flipped 90-degree) connected through the butadiyne linker.
- Both rings are non-aromatic.
- No charged species has been studied.

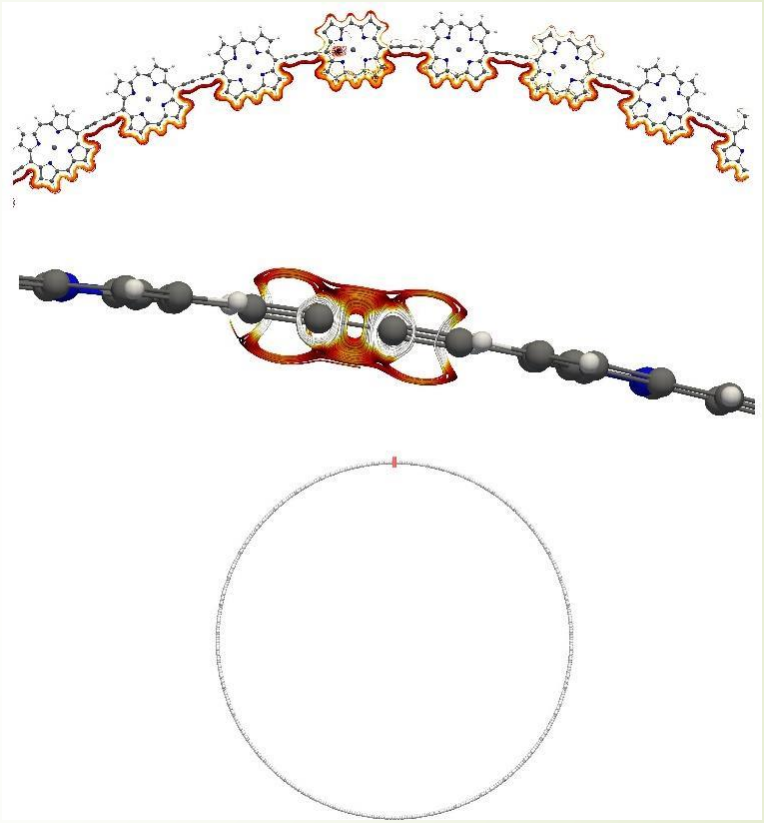


Figure 16. P40 rings of Nanowheel 1 & Nanowheel 2

BAND GAP IN THE CHARGED SPECIES

- Removing an electron from HOMO creates a hole in the valance band leading to a small HOMO-LUMO gap
- The conduction and valance band are almost mirror images
- The charged species of the cross-belts could not studied.
- For the same reason oxidized nanowheels could not be studied.

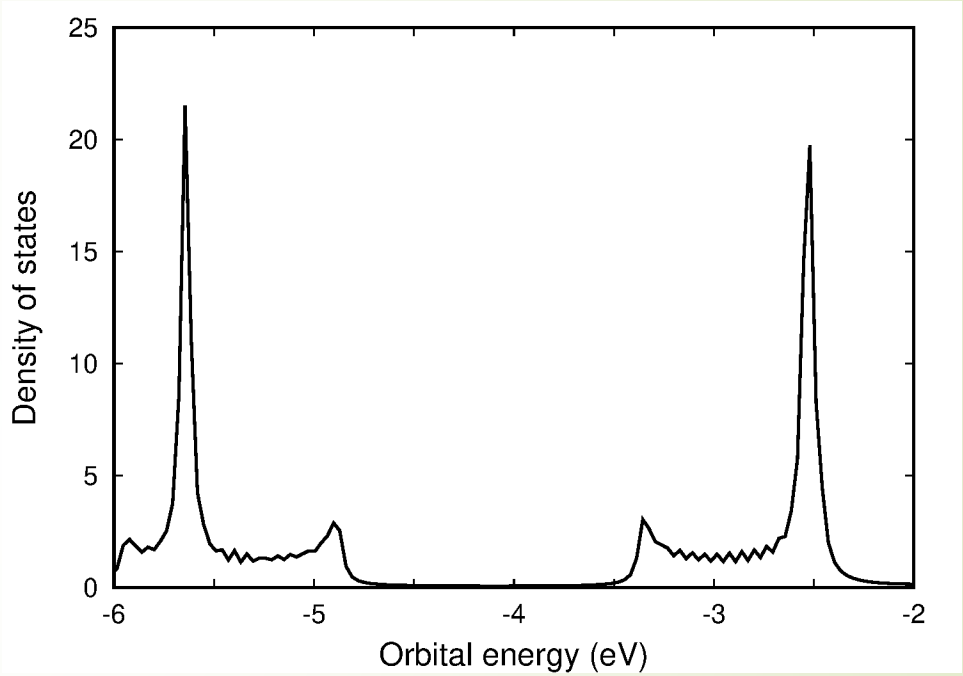


Figure 17. Density of states for the Nanowheel 2. The orbital energy of the HOMO is −4.88 eV and the orbital energy of the LUMO is −3.36 eV.

THE PSEUDO-π MODEL APPROACH

Three pseudo-π approach systems:

1. We have removed all the existing H-atoms and then the carbon and nitrogen are replaced with H-atoms. The zinc atoms are replaced with the Be atoms.
2. The second system is a free-base pseudo-π system. In this case, we have mimicked the case 1 with the exception that the Zn-atom were replaced with two H-atoms.
3. In the third system every thing was same with the exception that instead of replacing Zn-atoms with anything, we got ride of the Zn-atoms in the system. Thus, it is a dehydro system.

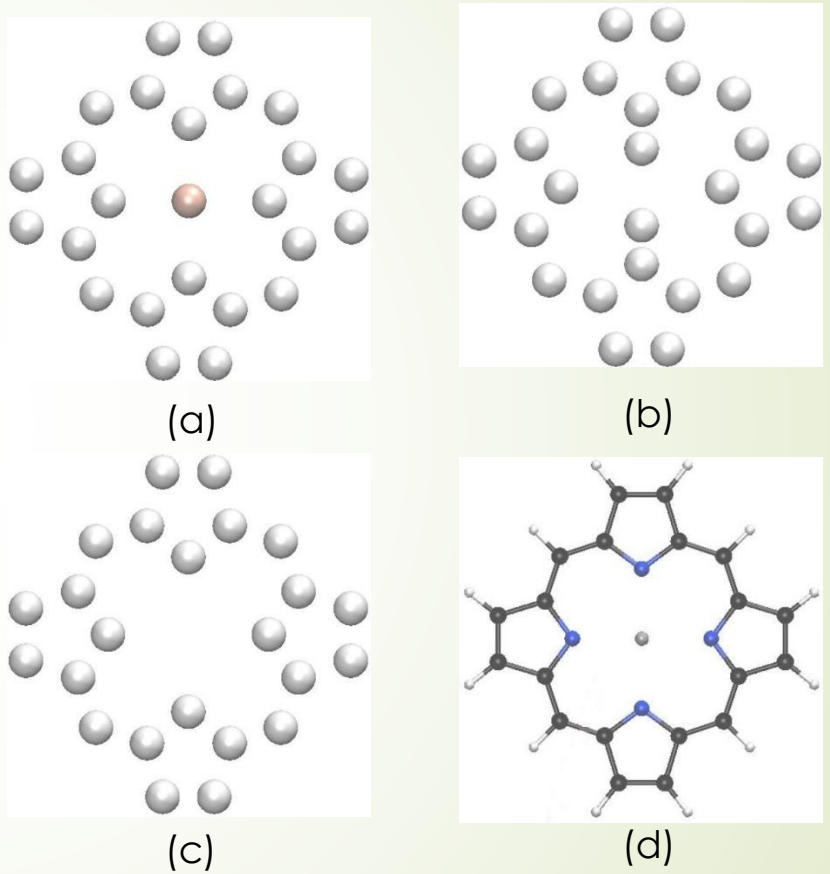


Figure 18. (a), (b) & (c) are three Pseudo-π models and (d) is all electron system of a single porphyrin

P. W. Fowler, E. Steiner, Chem. Phys. Lett. 2002, 364, 259–266

THE PSEUDO-ΠΤ MODEL APPROACH TESTED ON SINGLE UNITS

- Initially, pseudo-π method approach was tested on single Zn-based porphyrin units
- Dehydro pseudo-π model cannot be used.
- Pseudo-π method approach can be applied on porphyrins
- The results look promising.
- This approach is then employed on our nanowheel 1 & nanowheel 2

Table 2. Global ring current strengths and their diatropic and paratropic contributions

Plane	Diatropic	Paratropic	Net
SINGLE-PORPHYRIN UNIT	30.40	-3.67	26.73
PSEUDO-BE-PORPHYRIN	25.62	-0.00	25.62
PSEUDO-ZN-PORPHYRIN	27.72	-0.00	27.72
PSEUDO-FREEBASE-PORPHYRIN	23.14	-1.18	21.95
PSEUDO-DEHYDRO	135.3	-16.37	118.9

THE PSEUDO-ΠΤ MODEL ON LARGE PORPHYRINOIDS

- Pseudo-π method approach can be applied on large Porphyrin nanostructures
- Be Pseudo- π model is the best for the nanowheels
- It is cost effective approach
- Pseudo-π method gives same magnetic response as all-electron calculations
- Be Pseudo- π model approach slightly underestimates the aromaticity of Zn-porphyrinoids

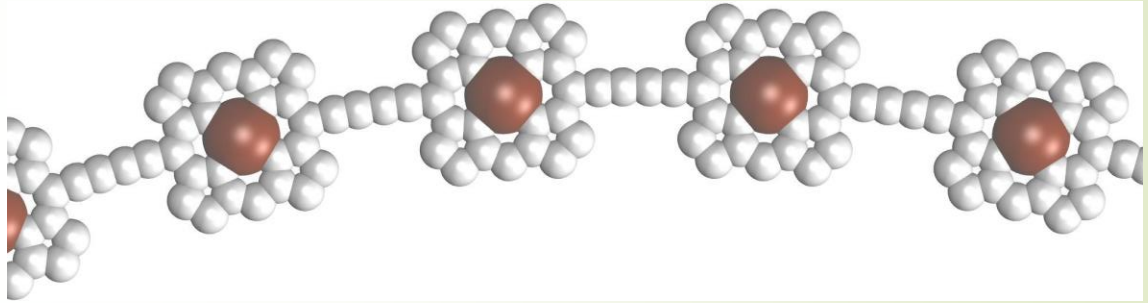


Figure 19. Be Pseudo-π model on nanowheel 1

ACKNOWLEDGEMENTS

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Thank you for your attention

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