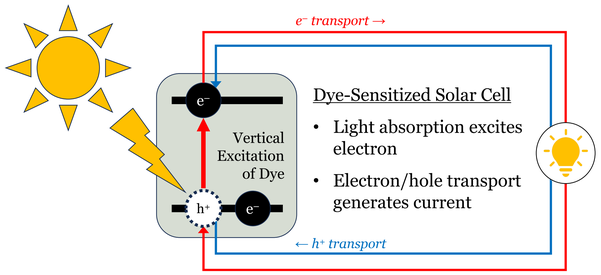
Tuning the Optical Band Gap in Al-Doped Porphyrin Complexes for Artificial Photosynthesis via Axial Donor-Acceptor Functionalization

Carlos H. Vargas III and Dominic A. Sirianni

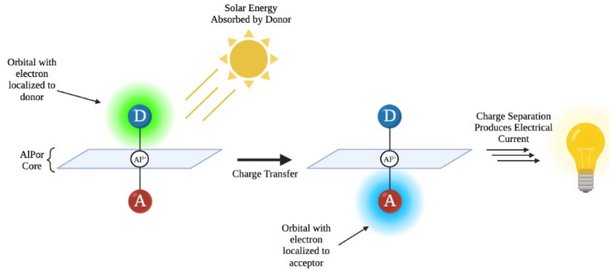
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DAEMEN UNIVERSITY
DEPARTMENT OF NATURAL SCIENCES

Project Overview



- Challenge: e^-/h^+ recombination can prevent current flow in any solar cell, regardless of dye choice
- Aluminum(III)-doped porphyrin ring (AlPor) systems w/ axial e^- donating groups (D) & e^- withdrawing groups (A) have shown promise as effective dyes which can encourage charge transport[1]



Questions:

- What properties of donor & acceptor groups encourage charge transfer (CT) excitation?
- What can we learn from this to help guide design of new "artificial photosynthetic" agents?

Computational Approach

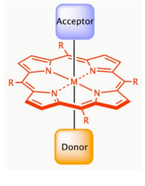
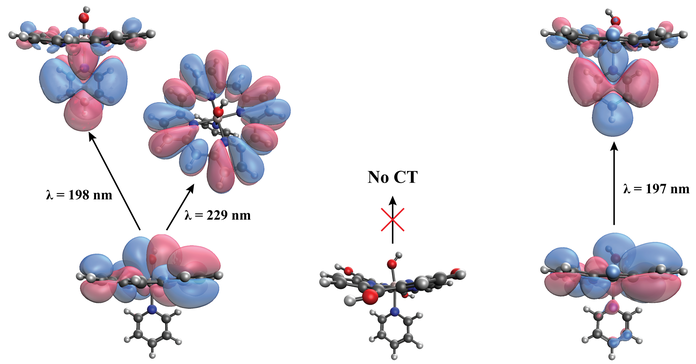


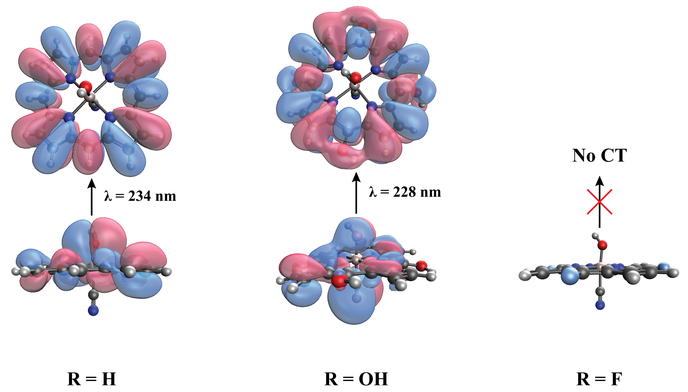
Figure adapted from Fig. 1 of Ref. 1

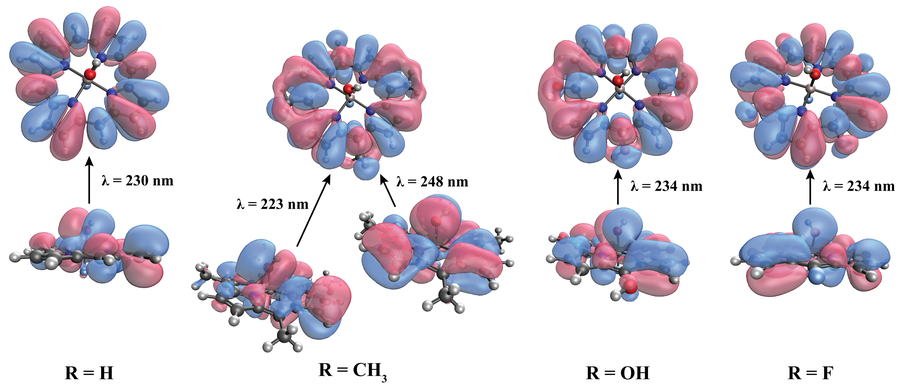
$$\lambda = \frac{hc}{\Delta E\,(1 \rightarrow 2)}$$

- Geometries optimized @ B3LYP/6-311++G** w/ Q-Chem 5.3
- Orbitals visualized w/ IQMol 3.0.1
- Likely transition orbitals identified by evidence of charge transfer excitation
- Substrate scope inspired by Ref. 1:
  - D = OH, CH_3
  - A = F, CN, C(=O)F, pyridinium
  - R = H, CH_3, OH, F

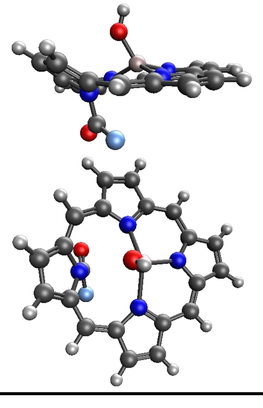
Systems with Observed Charge-Transfer Excitations



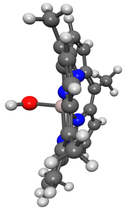




Optimization Catastrophes



- Acyl acceptors always left Al^{3+} core, regardless of R or D
  - some bonded to porphyrin π system (left)
  - some acyl groups left entirely (below)



Vacation →
← Work

- Defects also formed during opt's of R/CH_3/F

Conclusions

Geometric Observations

- R = OH, CH3: Porphyrin heavily distorts into nonplanar Pringle shape regardless of D/A
- R = H, F: Porphyrin distorts into nonplanar bowl shape, ligand which is more strongly σ-withdrawing "rides" in the bowl

Electronic Observations

- Increasing non-planarity of Por. ⇒ more MOs fully delocalized
  - ⇒ Fewer CT excitations (both axial & equatorial)
- R/OH/F:
  - HOMO-1 always "localized" to D + AlPor, LUMO+4 always localized to Por. "perimeter"
  - Dense manifold of shorter-λ transitions b/t D–Al^{3+}–A "core" to "perimeter" when R=CH_3, F
- When axial ligand is π-donating (A = CN, Pyr^+), MOs significantly delocalized, significantly fewer CT transitions
- A = Pyr^+ only system demonstrating axial D→A CT

References

1. Zarrabi & Poddutoori, *Coordination Chem. Rev.* 429, 213561 (2021)

Acknowledgements: The authors wish to acknowledge funding support from Daemen University via a Think-Tank grant (#1-059050-51520) and computational support provided by the Palmetto Supercomputing Center made available through the MERCURY consortium and the National Science Foundation (Grants CHE-1626238, CHE-1662030, and CHE-2018427).

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