PBF has the highest hyperpolarizability (6.856 ×10⁻ ³¹ cm⁵ esu⁻ ¹) for NLO applications, PBFz shows the highest dipole moment (0.026 D) for D

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Structural modification of porphyrin to accelerate the electron donor nature; A physicochemical and spectral study

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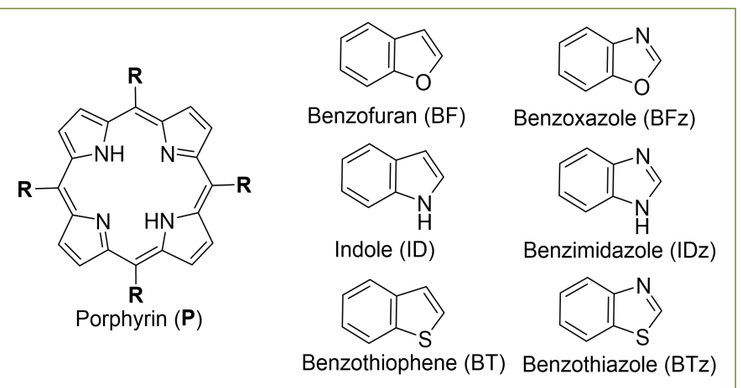
INTRODUCTION & AIM

Solar energy is a clean, infinite solution in light of growing energy demands and climate challenges. Porphyrins are highly conjugated, macrocyclic compounds composed of four pyrrole rings linked by methine bridges, forming a planar, aromatic 18 π-electron system. Because of their adaptability, affordability, and tunability, remarkable light-harvesting capabilities, thermal stability, dye-sensitized solar cells (DSSCs) have become an available substitute for traditional silicon-based photovoltaics. They are perfect for photovoltaic and catalytic applications because of their distinct donor –acceptor behavior. By adding electron-donating or Withdrawing groups such as BF, BFz, ID, IDz, BT, BTz to Porphyrin (P) structures, HOMO–LUMO gaps can be adjusted, charge separation can be improved, and reactivity can be increased. In addition to solar cells, porphyrin-based catalysts exhibit great promise in environmental remediation, CO_2 /N_2 reduction, and water splitting. This work offers thermochemical, spectral, and optical insights into modified porphyrins to identify structure–property relationships that optimize catalytic efficiency and DSSC performance. Our research opens the door for next-generation multifunctional materials in applications related to green chemistry and renewable energy.

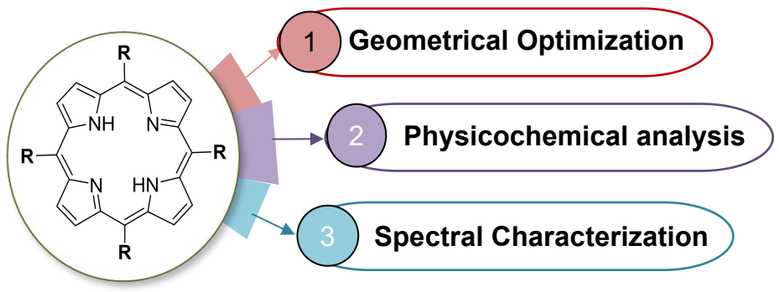


METHOD

Used software

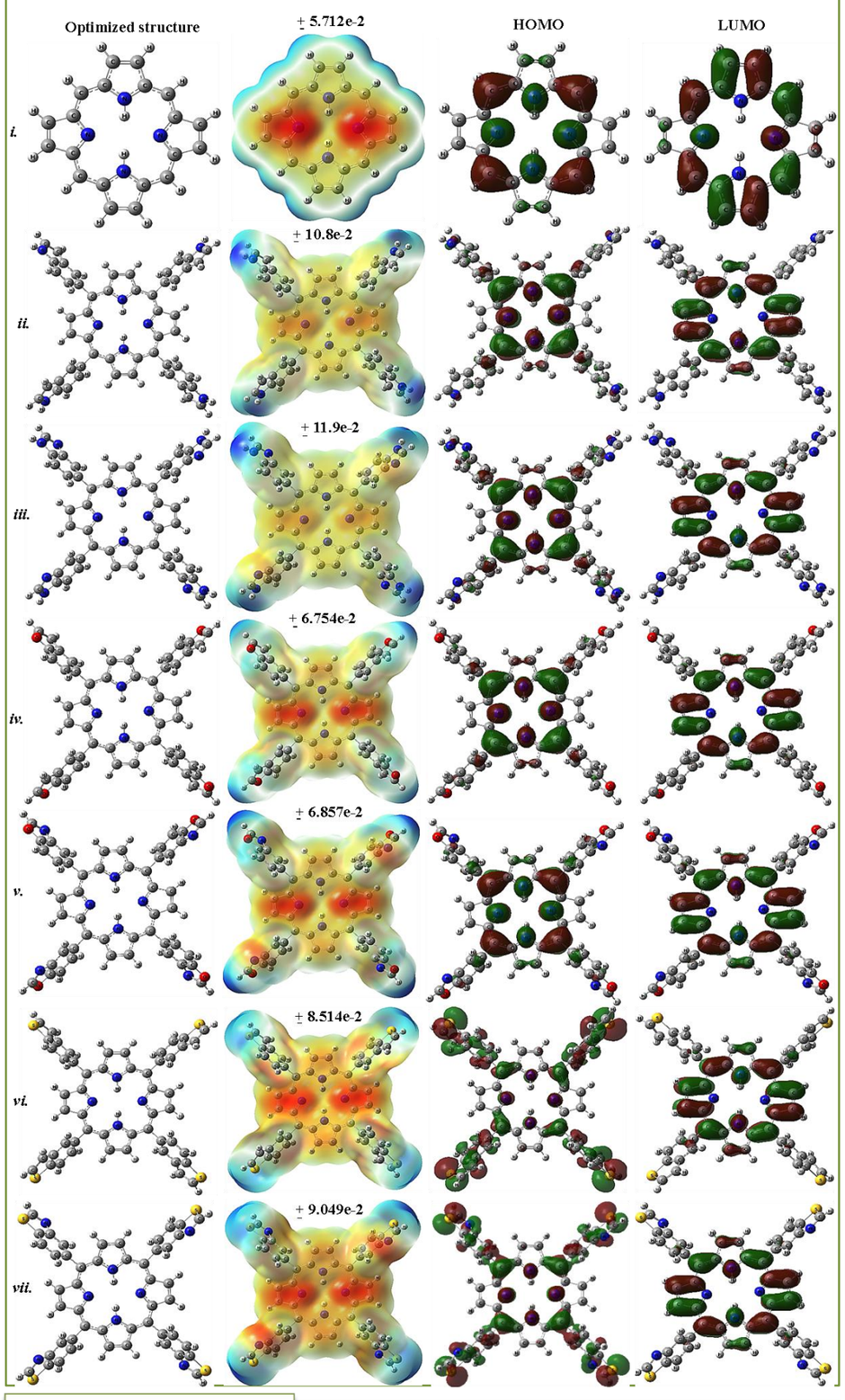
Geometry optimization
1. Gaussian 16W

- DFT method
- B3LYP functional
- 6-31+G(d,p) basis set
- Multiwfn 3.8 software (DOS plot and TDM Graphs)

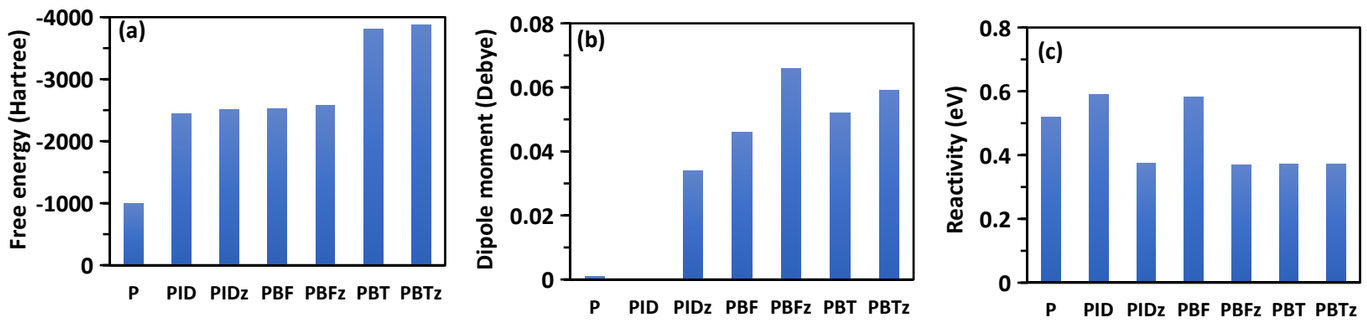


3. RESULTS & DISCUSSION

3.1. Electronic feature



3.2. Thermodynamic (a) & (b) and orbital (c) & (d) analysis



3.3. Spectral analysis

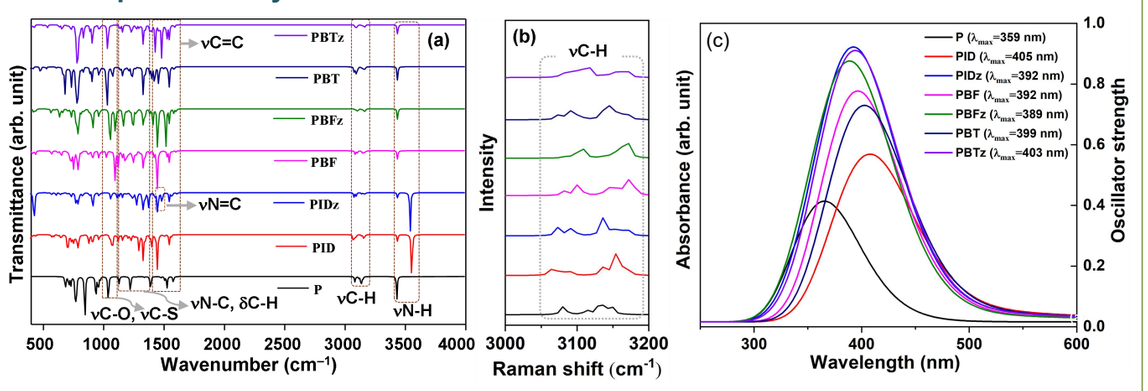
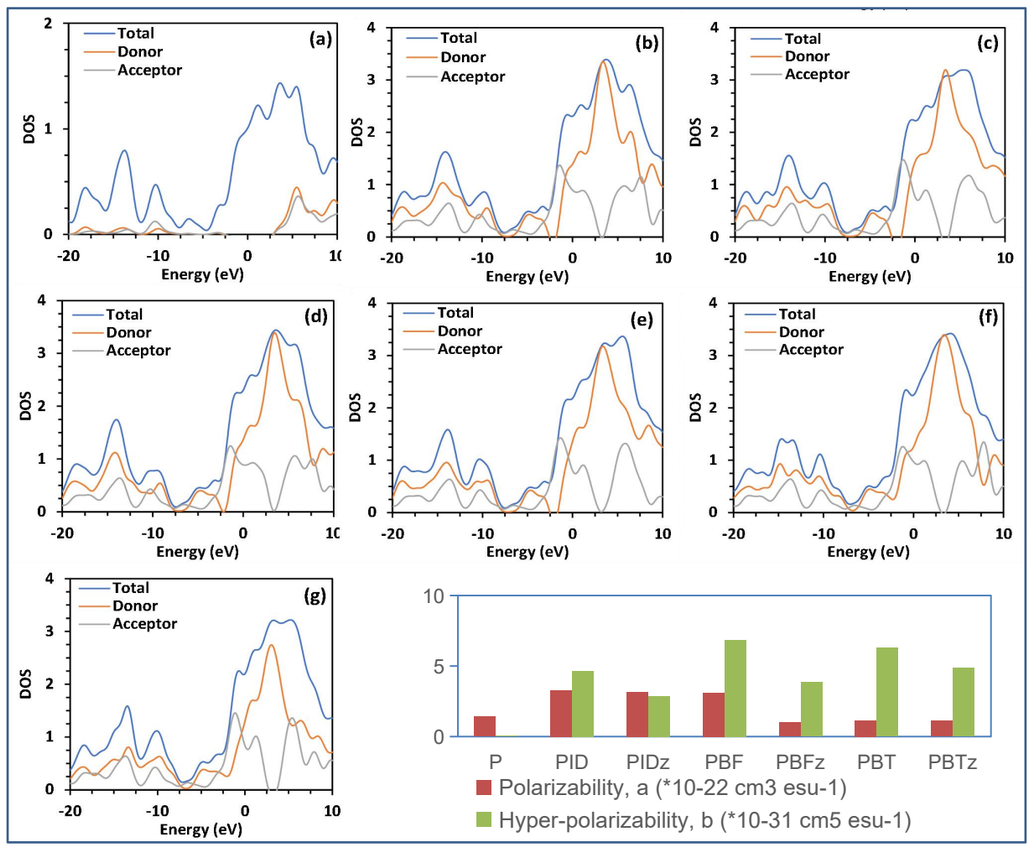
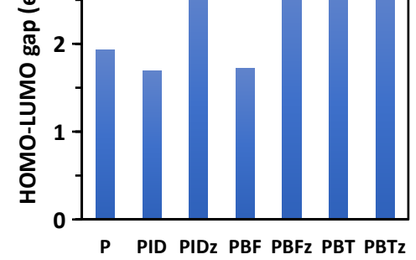


Fig (a) FT-IR, and (b) Raman (c) Uv spectra of the studied compounds.

3.3. (i) Density of state and (ii) TDM graphs of (a) P, (b) PBF, (c) PBFz, (d) PID, (e) PIDz, (f) PBT, and (g) PBTz.





(ii)

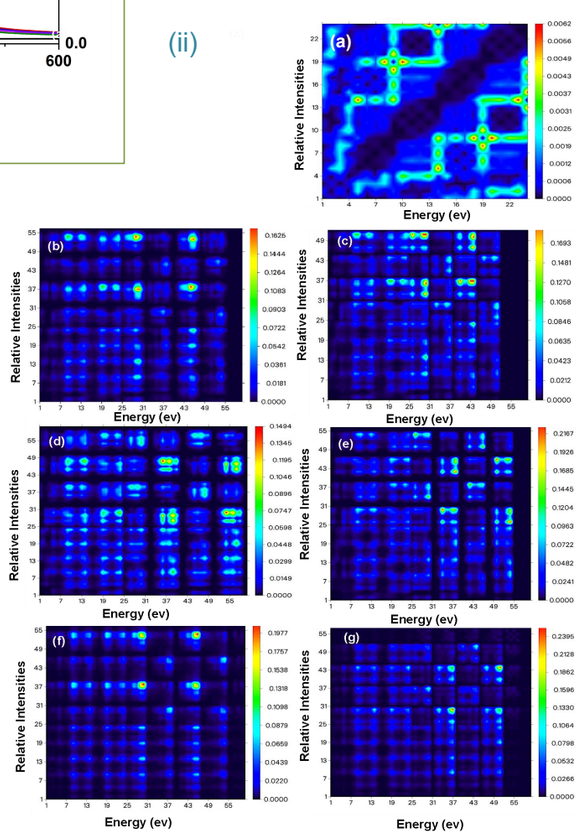


Table 1.Calculated HOMO–LUMO (Egap), initial singlet excitation energy (Eopt), and exciton binding energy (E_b)

Compounds	E_{opt}	E_{gap}	E_b
P	3.448	1.927	1.521
PID	3.061	1.691	1.37
PIDz	3.061	2.67	0.391
PBF	3.061	1.719	1.342
PBFz	3.061	2.703	0.358
PBT	3.061	2.703	0.358
PBTz	3.061	2.689	0.372

PBF excels in hyperpolarizability (6.856 ×10⁻ ³¹ cm⁵ esu⁻ ¹) for NLO, PBFz in dipole moment (0.026 D) for DSSC, and PID in polarizability (3.272 ×10⁻ ²² cm³ esu⁻ ¹) for electronics.

CONCLUSION

This study highlights PBF and PID as the best doner, which help to build effective donor-acceptor systems for next-generation solar cells. And PBFz and PIDz as top-performing porphyrin derivatives for enhanced DSSC efficiency and catalytic activity. Thermochemical analysis reveals their high stability and strong polarity; FMO and DOS results confirm effective charge transfer and separation. PBFz exhibits the lowest exciton binding energy (0.358 eV) and highest oscillator strength, ensuring superior light-harvesting. NBO analysis shows strong donor-acceptor interactions and high electron delocalization. These insights affirm the impact of structural tuning in optimizing porphyrins for next-generation solar and catalytic systems.

REFERENCES

1 . Y. Li *et al*, *Molecules*, doi:10.3390/molecules27061800. **2** . A. Hagfeldt, G. Boschloo, L. Sun, L. Kloo, and H. Pettersson, *Chem Rev*, doi: 10.1021/CR900356P/ASSET/CR900356P.FP.PNG_V03