

Spin Multiplicity Dependent Electronic and Optical Properties of Cobalt Phthalocyanine: A DFT Study

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Introduction

- Cobalt phthalocyanine (CoPc; Figure 1) has been explored for its application in various research relating to catalysis,¹ solar cells,² efficient laser dyes, electronic and optoelectronics devices.³
- Our work explores how electron spin influences the electronic and optical behaviour of CoPc, providing crucial understanding for its use in energy applications.
- This work is linked to United Nations Sustainable Development Goal 7 (Affordable and Clean Energy).

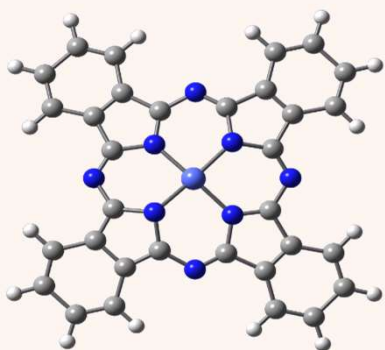


Figure 1: Structure of CoPc

Computational Methodology

- Various CoPc spin multiplicities (doublet, quartet, sextet) were studied using B3LYP and CAM-B3LYP with 6-311G(d).
- Electronic properties [orbital energies, ionization potential (IP), electron affinity (EA), electronegativity (χ) and chemical hardness (η)] were computed from the energies of the neutral, cationic and anionic molecules (Table 1).

Spin	IP	EA	χ	η
Doublet	4.08	4.35	4.35	0.27
Quartet	14.93	1.70	8.32	6.62
Sextet	15.24	1.80	8.52	6.72

Table 1: Electronic properties for various spin states using B3LYP/6-311G(d)

- TD-DFT was used to study the optical properties.
- IP and EA were calculated from the ground state energy of the neutral, cationic and anionic molecules using the equations below:

$$IP = E_{\text{cation}} - E_{\text{neutral}}$$

$$EA = E_{\text{neutral}} - E_{\text{anion}}$$

Results

- rCo-N is similar for all spin states and longer than the experimental value (Table 2).

Parameter (r / pm; $\angle$ / °)	EXP ⁴	SPIN MULTIPLICITY		
		Doublet	Quartet	Sextet
rCo-N	1.931	1.968	1.989	1.987
$\angle$ N-Co-N'	90.0	90.0	90.0	90.0
rC-N(ring)	1.376	1.377	1.371	1.379
rC-N(linker)	1.328	1.326	1.327	1.352
$\angle$ N(ring)-C-N(linker)	127.9	127.6	127.5	127.4

Table 2: Parameters calculated at B3LYP/6-311G(d)

- The MOs of CoPc were analysed by visualizing the HOMO and LUMO orbitals (Figure 2).
- The HOMO is centred on N atoms adjacent to the aromatic macrocycle; the LUMO is delocalized across Co and the Pc ligand.

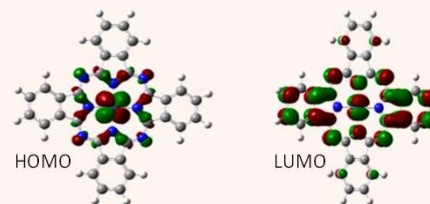


Figure 2: HOMO and LUMO orbitals for CoPc calculated using B3LYP/6-311G(d)

Optical Spectra

- Two energy bands were observed: the Soret (B) band ~380-415 nm and Q band ~530-630 nm.
- Q band position is greatly affected by spin state.

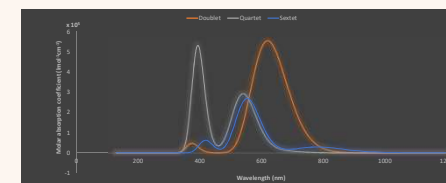


Figure 3: Absorption spectra of CoPc (CAM-B3LYP/6-311G(d))

Conclusions

- The peak width / position in optical spectra of CoPc is affected by the magnetic interactions among unpaired electrons. This is important for optoelectronics applications.
- Of the investigated spin states, the doublet shows the best combination of IP, EA, χ , η and shift in peak positions.

References

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