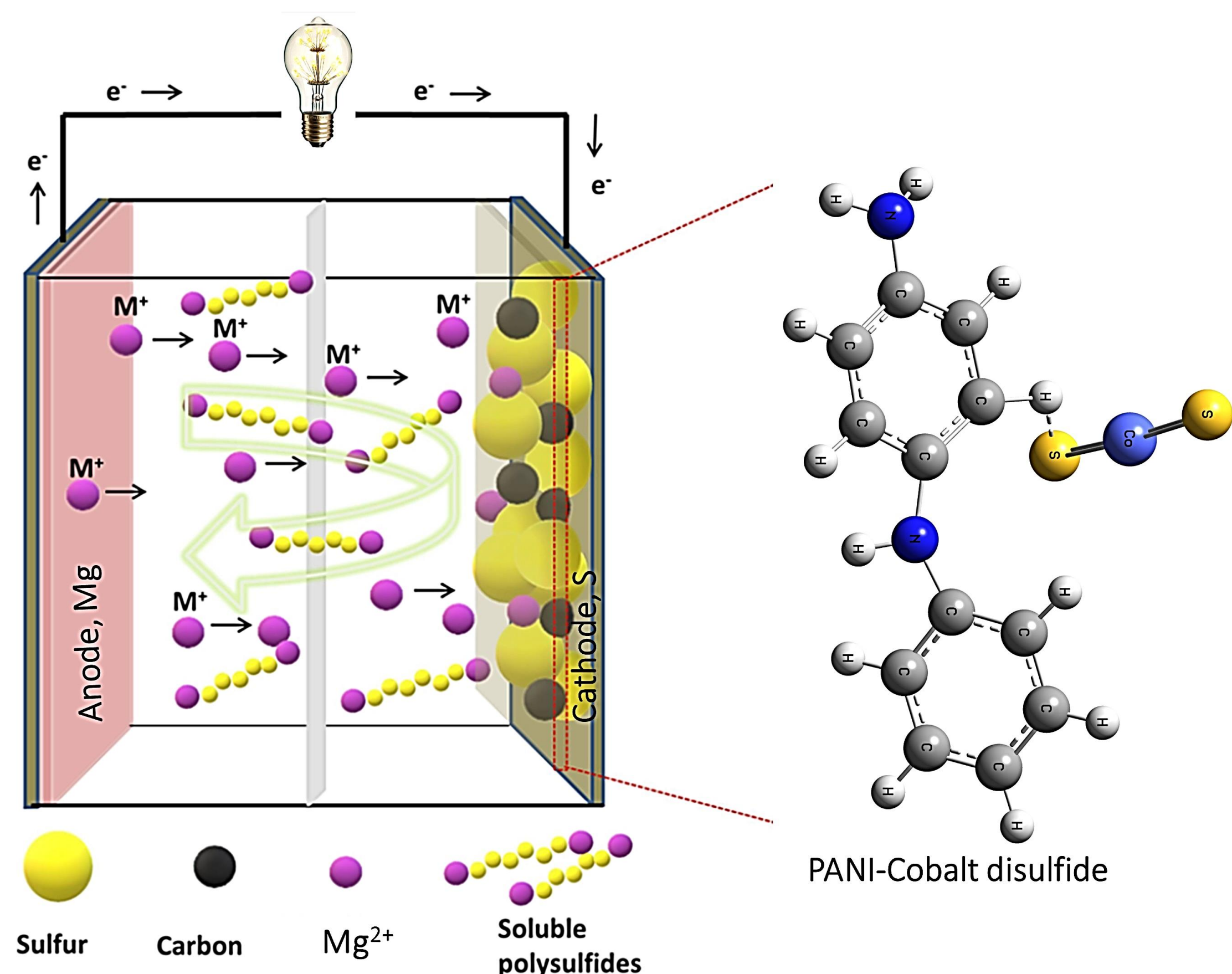


Hassan O. Shoyiga, Msimelelo Siswana

Graphical Abstract



Scheme 1. Mg-S battery with modified cathode

Introduction

Magnesium-sulfur batteries offer improved theoretical energy density, material availability, and environmental compatibility. However, practical applications face challenges like polysulphide shuttle effects, slow Mg^{2+} transport, and interfacial instability. Electrode modification is crucial for optimal charge transport and performance. This study uses first-principles calculations to evaluate electronic interactions between polyaniline (PANI)-cobalt disulfide (CoS_2) and their impact on charge transport and MgS_2 oxidation.

Methodology

- Molecular optimisation, followed by computational analysis
- DFT calculations done with the B3LYP functional and 6-311G (d,p) basis set
- Koopmann's theorem for chemical reactivities
- All calculations were carried out using the Gaussian 09 software package and GaussView
- Binding energy was estimated using Eq. (1):

$$E_{B.E} = E_{complex (PANI/CoS_2)} - E_{PANI} - E_{CoS_2} \quad (1)$$

Results and Insights

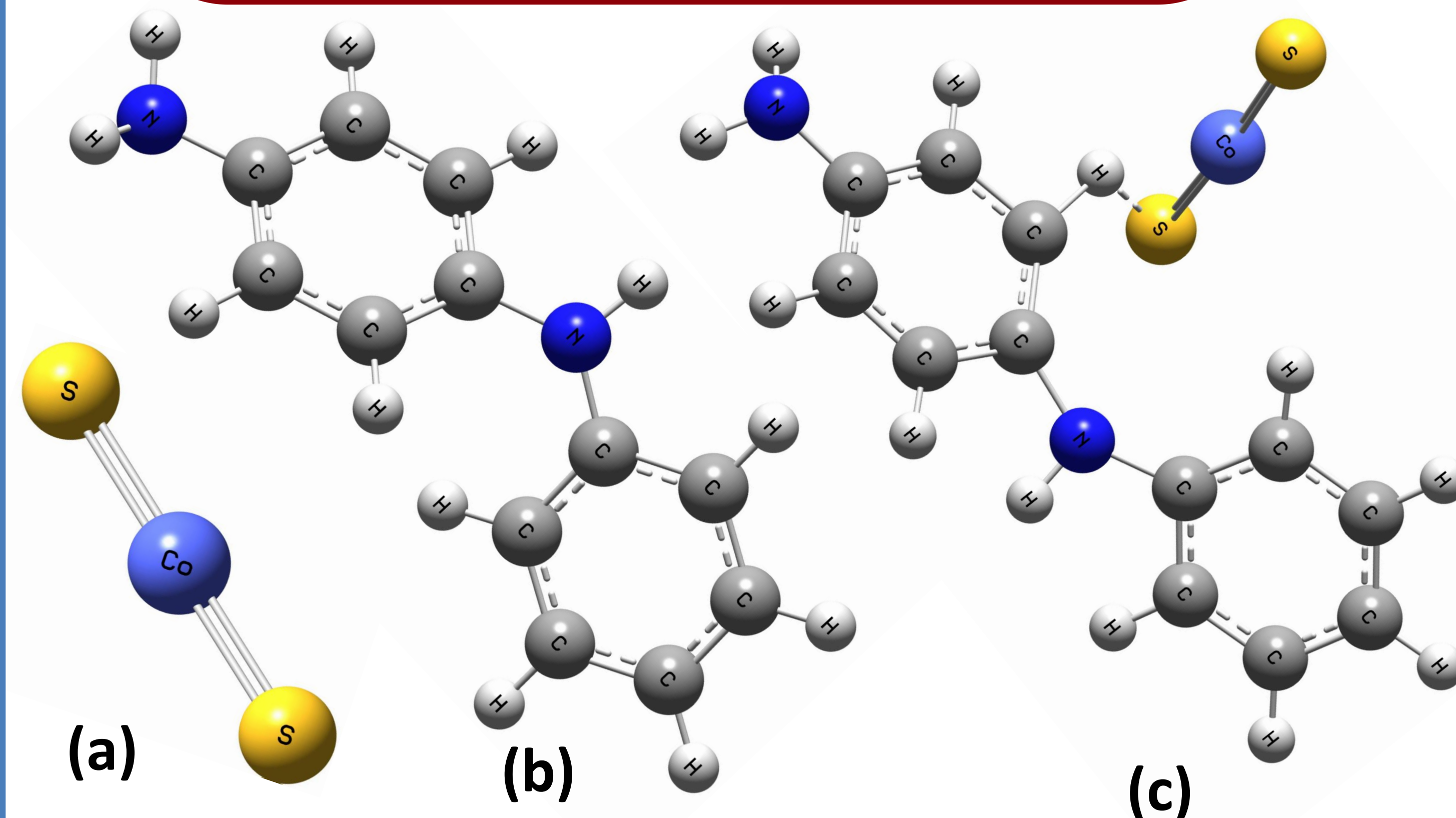


Fig 1. Optimised structure of: (a) Cobalt disulfide, (b) Polyaniline and (c) PANI- CoS_2

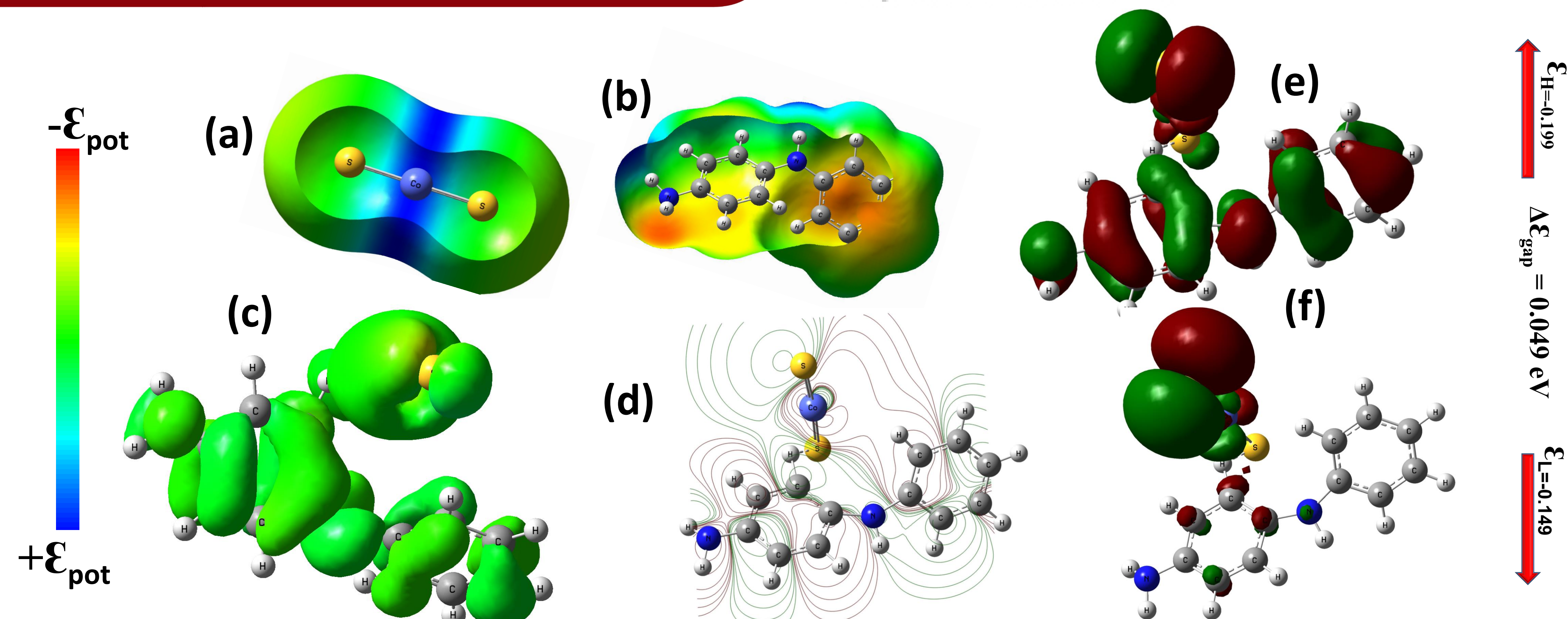


Fig 2. Electrostatic potential (ESP) of: (a) CoS_2 , (b) PANI, and (c) PANI- CoS_2 , (d) Electronic contour mapping of PANI- CoS_2 , (e) HOMO, and (f) LUMO of PANI- CoS_2 .

Optimised molecules, Fig.1 (a-c), employed in DFT calculations are stable, with significant polarity, and a high electron-donating ability (Fig. 2c-d). The low E_{gap} suggests optoelectronic activity, with the potential for increased binding affinity and charge transfer (Fig. 2e-f). Their chemical hardness and softness values suggest good kinetic stability (Table 1).

Table 1. Summary of the chemical reactivity descriptor PANI- CoS_2 composite

Reactivity descriptor	Global Electrophilicity Index (ω)	Electronic chemical potential (μ)	Chemical Softness (S)	Global Hardness (η)	Ionisation Energy (I)	Electron Affinity (A)	Binding Energy ($E_{B.E}$)
PANI/ CoS_2	0.622 eV	-0.0175 eV	40.601 eV	0.0246 eV	-0.149 eV	-0.199 eV	-50.351 eV

Conclusions

The optimised molecules show significant stability, with the potential for increased charge transfer for enhanced battery performance.

References

1. D. Sharma, T. Singh, J. Molec Liquids. 239 (2019), 111528.
2. O. E. Fayemi, H. O Shoyiga et. al. Sci. Rep. 15 (2025) 10865.

Acknowledgements

HS and MS are grateful to Walter Sisulu University's research directorate for their generous financial assistance for the postdoctoral fellowship and the availability of research facilities.