

Synthesis, Structure and Characterisation of a New Class of Nickel Dithiolene

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Introduction

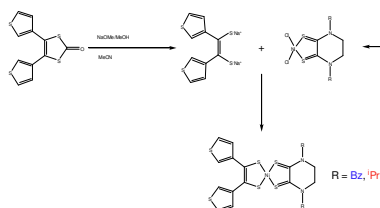


Fig 1: Route to [Ni(R_pipdt)(b-3ted)].

Nickel dithiolenes are attractive building blocks for incorporation into conjugated polymers due to their aromaticity and facile reduction (*n*-doping).¹ Reports of superconductivity² and of non-linear optical (NLO) properties³ further support research into this field. Pendant thiophene groups have previously been shown to homo-polymerise and are useful ligands for such systems.^{4,5}

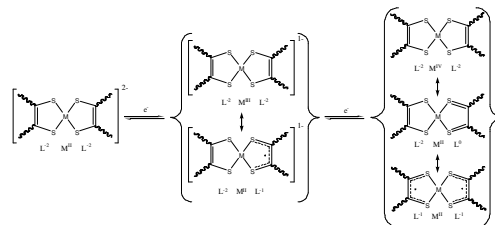


Fig 2: Redox processes and resonance forms of nickel dithiolenes.⁶

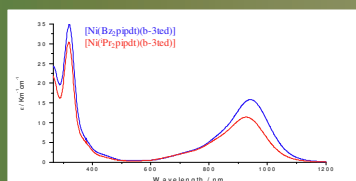


Fig 3: UV/Vis/NIR data.

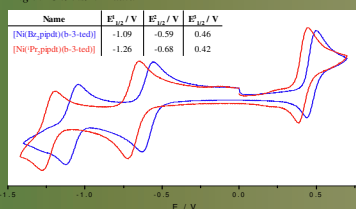


Fig 4: Reversible redox processes.

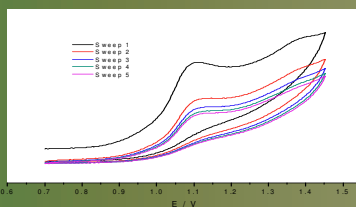


Fig 5: Irreversible oxidations of [Ni(Bz_pipdt)(b-3ted)].

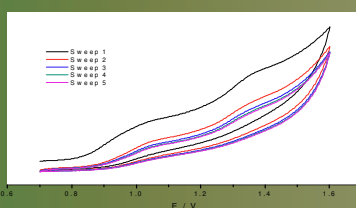


Fig 6: Irreversible oxidations of [Ni(Pr_pipdt)(b-3ted)].

• **Synthesis** has been optimised and characterisation by ¹H NMR, and elemental analysis has show clean, stable products.

• **UV/Vis/NIR** spectroscopy shows an absorption in the NIR region attributed to LLCT and is strongly dependent on the nature of the R groups.

• **Cyclic voltammetry** shows five one-electron redox processes for both complexes:

- Two reversible processes at negative potentials, assigned to [MLL'] 2-/1-, [MLL'] 1-/0.

- A reversible process at a positive potential, assigned to [MLL'] 0/1+, indicating the formation of a stable cation.

- Two irreversible peaks above 1 V, assigned to oxidation of the thiophene groups, though no evidence of polymerisation was observed under the conditions chosen.

• **SC-XRD** shows the packing structure to be variable with the nature of the R groups. The central Ni-S core is essentially square planar in both complexes and bond lengths of the dithiolenes confirm the [Ni(dithione)(dithiolate)] nature of the complex.

• **DFT** calculations suggest that, although the frontier orbitals are spread over the whole molecule, the R₂pipdt has a greater HOMO contribution and the b-3ted a greater LUMO contribution.

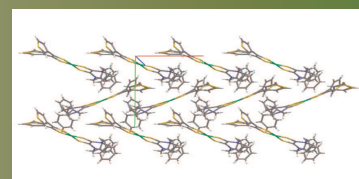


Fig 8: Packing structure of [Ni(Bz_pipdt)(b-3ted)].

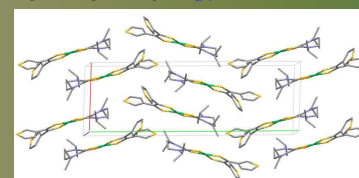


Fig 7: Packing structure of [Ni(Pr_pipdt)(b-3ted)].

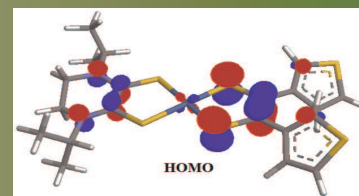


Fig 9: DFT calculation of HOMO orbital.

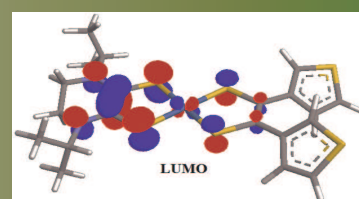


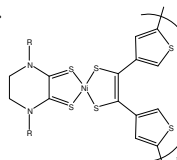
Fig 10: DFT calculation of LUMO orbital.

Conclusions

- A synthetic route to a range of tuneable asymmetric dithiolenes has been optimised.
- Such complexes show potential for oxidative polymerisation.
- Crystal structures combined with DFT calculations suggest application as tuneable conductive materials.

Future Work

- Test conductivity and first-order hyperpolarisability for use as NLO materials.
- Investigate homo- and hetero-polymerisation and thin film formation for field-effect transistor studies.



Acknowledgements

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References

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