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Synthesis and Physical Properties of Hetero-substituted-HATNs and their Cu(I) and Re(I) Complexes

A thesis presented in partial fulfilment of the requirements for the degree of Doctor of Philosophy in Chemistry at Massey University, Palmerston North

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“An expert is a person who has made all the mistakes that can be made in a very narrow field.”
– Niels Bohr

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Abstract

The electron deficient hexaazatrinaphthalene compounds are of interest for photovoltaic (PV) and molecular devices. These molecules contain multi phenazine (a common dye chromophore) centres that allow coordination of metals, forming complexes that have been shown to have photophysical properties that could be commercially valuable. HATNAs have been investigated for use in molecular devices; including liquid crystals (LCs), light emitting diodes (LEDs), PVs, and field effect transistors (FETs) by a variety of groups.

The initial goal of this thesis was the synthesis of mixed or 'hetero'-HATNs. Preliminary investigations leading into the synthesis of HATNAs showed a number of problems associated with solubility, purification, and stability of these compounds, however a method was established and six hetero-HATNs, HATN-4Me, HATN-4Br, HATN-2Me, HATN4Br2Me HATN-2Br and HATN-4Me2Br, were synthesised and carried throughout the thesis. The rhodizonic acid route and its reactions with the appropriate diaminobenzenes followed by oxidation with nitric acid and then further reactions with diaminobenzene was considered the best.

The crystal structure of one of the possible intermediates for HATN production, PTK-2Me which is based on a 1,2,3,4-phenazinetetrone displays the presence of a gem-diol equilibrium on one of the rings which is no longer aromatic. The crystal structure of PKH-2Me (PKH = 2,3-dihydroxyphenzine-1,4-dione) which is a precursor to the PTK-2Me intermediate shows the C-OH bonds are shortened due to the partial double bond character due to a shifting of the equilibrium between a ketone and a hydroxyl group. The crystal structure of HATN-4Me shows all of the aromatic rings to be mostly planar with slight distortion. The MALDI mass spectra for each of the electron deficient HATNs displays a band due to $[M+2]^+$ cations which is unusual and possibly formed by a $[M+2H^+ + e^-]$ species.

Physical properties of the six HATNs were investigated using UV/Vis, Raman and IR spectroscopies. They were tested as the electron-transport-material in a field effect transistor. It was found that HATN-4Br had the highest electron mobility of 8.13 x 10^4 $\mathrm{cm^2V^{-1}s^{-1}}$ and this was obtained after vacuum deposition onto a substrate rather than a solution processed deposition. However as it has a high resistance it is not suitable for a FET device.

The HATNs all display first reduction potentials at -0.9 V with a second at about -1.4 V. They are all quite close and do not appear to follow the expected trend according to the nature of the functional groups.

The HATNs coordinate to rhenium to form A and S isomers which are difficult to isolate. The HATN-1Re complexes display similar physical properties. When two rhenium atoms are added (HATN-2Re) there is a noticeable red-shift in their absorption spectra (100 nm). Crystal structures of HATN-4Me-1ReA and HATN-4Me-1ReS and HATN-2Me-2ReS were obtained and these show twisting of the HATN core up to 13˚. These structures showed the π-π stacking ability of the HATN complexes ranging from 1 to 3 ring overlaps as well as solvent interactions.

Copper willingly binds to all three bidentate hetero-HATN sites and has the unusual property of a colour change between the solvents acetonitrile and chloroform. The reason for this colour change is discussed and found possibly to be due to copper dissociation.

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