SYNOPSIS

Quest for molecular materials exhibiting a great variety of interesting and useful properties is one of the major areas of research today. Such properties include electrical conduction, magnetism and nonlinear optical effects. Magnetic molecular materials have been projected as having great significance in the field of molecular electronics, memory devices and telecommunication. Molecules are predominantly diamagnetic with a closed shell electronic configuration. However, many transition metal complexes and organic free/ion radicals have unpaired electrons. The spin interactions in the solid state of these systems are mostly antiferromagnetic. From a technological point of view as well as to obtain a fundamental understanding of the magnetic phenomena, it is important to design such molecular materials with ferromagnetic couplings and ultimately bulk ferromagnetism.

This thesis presents our studies on the problem of molecular magnetism, along two different approaches: i) investigation of the nature of spin coupling in conjugated and non-conjugated organic di and multiradicals using semiempirical computational methods, and ii) experimental design of new approaches to achieve cooperative magnetic interactions in molecular materials. The thesis is divided into five Chapters. We describe below salient features of the contents of each Chapter.
Organic diradicals constitute the basic units in the topological models. The basic features of these diradicals are the ground state spin and the singlet-triplet energy gap. The zero field splitting (ZFS) parameters D and E are the signatures of triplet diradicals. Earlier computational work has mainly addressed the problem of predicting the ground state spin and the singlet-triplet energy gap. The ZFS parameters, on the other hand, have been rather difficult to compute in good agreement with experimental values. Semiempirical AM1 calculations (including limited CI) have been shown to provide fairly accurate predictions of the ground state spin in organic radical systems. In Section 3, using computations on a large set of organic diradicals, we demonstrate that open shell RHF AM1/CI procedure provides a good theoretical estimate of their zero field splitting parameters. These calculated ZFS parameters are found to be in much better agreement with experimental data than the earlier computational predictions. The ground state spin determination of tetramethyleneethane (TME) has been a notable case of conflict between theory and experiment. While experimentally it was shown that TME has a triplet ground state with a likely nonplanar geometry, theoretical calculations at various levels have consistently predicted a singlet ground state at planar as well as nonplanar geometries. However, recent high level ab initio/CI calculations have shown that TME has a weakly stabilised triplet ground state at a twist angle of about $50^\circ$. In Section 4, we provide our detailed semiempirical computational study of TME which showed that CI calculations involving all the six $n$ MO's in the active space lead to a clear preference of a triplet state at twisted geometries. We have also examined the ZFS parameters of TME.
Our detailed analysis of the singlet-triplet energy gap in organic conjugated diradicals within the framework of a spin polarisation picture is presented in Section 5. We developed a simple algorithm to compute a spin coupling parameter in organic diradicals, and show that it is strongly correlated to the singlet-triplet energy gap in these systems and provides a means of predicting the latter.

Theoretical studies aimed at understanding the nature of spin coupling in non-conjugated organic radicals (with radical sites separated by saturated, sp$^3$ carbon atoms) are relatively sparse compared with the studies on their conjugated counterparts. Several recent developments including a model of a "ferrocarbon" proposed by Ovchinnikov suggests that spin interaction in non-conjugated organic radicals could be of fundamental interest. In Section 6, we describe our computational investigation of the ground state spin of model non-conjugated organic radicals. We present a systematic analysis of the spin coupling in terms of the relative orientation of spin orbitals in these systems. An appraisal of the ferrocarbon model as well as suggestions for viable experimental systems are also discussed.

CHAPTER 3. EXPERIMENTAL INVESTIGATION OF TWO APPROACHES TO MOLECULAR FERROMAGNETISM BASED ON THE SPIN POLARISATION PICTURE
In this chapter we propose two new approaches to ferromagnetism, both based on the notion of spin polarisation discussed in Section 1. Here the term spin polarisation is used in the sense that a and b spin show spatial preference over the molecular or polymer framework. In the first approach, charge transfer interactions in stacked organic complexes are envisaged, wherein the spin polarisation of diamagnetic spacer molecules/molecular ions are expected to lead to ferromagnetic alignment of spins on free or ion radicals. In the second approach based on a coordination polymer, spin polarisation in the bridging ligand species having π-conjugation, is expected to lead to ferromagnetic coupling of the metal ion spins.

Models for organic ferromagnets based on crystalline charge transfer complexes (as opposed to polymers) are of fundamental interest, since they offer insight into structural features that influence observed magnetic properties. We propose in Section 2, a new model combining basic aspects of charge transfer interaction and spin polarization. A mixed stack of ion radicals and diamagnetic molecular counterion spacers is considered. If the ion radicals stack such that they interact strongly with the same spin orbital of the spin polarised spacer, then the system would have overall ferromagnetic spin alignment along the stack. We have considered in this study, charge transfer complexes of dichlorodicyano-p-benzoquinonide (DDQ·) and hexacyanotrimethylenecyclopropanide (HCTMCP·) with tris(pyrroldino)cyclopropenium (TPC+) and N-methylphenazenium (NMP+) cations as diamagnetic spacers. Three of these new compounds were prepared by metathesis reactions and characterized. Since good quality
crystals could not be grown, structural information on the complexes could not be obtained. Magnetic properties of these materials were investigated by variable temperature electron spin resonance studies. While TPC-DDQ and TPC-HCTMCP showed Curie-Weiss antiferromagnetic behaviour, NMP-DDQ showed a more complex behaviour with antiferromagnetic, ferromagnetic and simple paramagnetic behaviours at different temperature regimes. Qualitative models to explain these observations are presented.

The main drawback of the polycarbene/polyradical systems based on the topological models for organic ferromagnets, is their chemical reactivity which often leads to low spin concentrations. If paramagnetic transition metal ions are used instead of carbon based radical systems, this problem could be circumvented. In a coordination polymer, if metal ion spin orbitals are in conjugation with the n - orbitals of the bridging ligand that has a suitable topological framework, then a system similar to the organic topological models could be visualized. In Section 3, we describe the synthesis, characterization and magnetic susceptibility measurements on three novel copper(II) complexes containing 4,5-dicyanoimidazole (DCI). Crystal structure analysis of the first complex prepared as a model system for the monomer unit revealed that the dicyanoimidazole does not coordinate to Cu(II). Since the counterion of the copper salt, namely the nitrate group was strongly coordinated to the metal ion in the complex, we prepared the next two systems, one from CuSO4 and the second, one from Cu(NO3)2 with an acidic buffer. In these two cases the ir spectral analysis indicated that the initial counterions are absent and that the DCI" is formed, perhaps
covalently linked to Cu(II). Crystal structural analysis of the complex prepared from CuSO$_4$ confirmed this. Magnetic properties of these complexes were studied using SQUID magnetometry. In all cases, only antiferromagnetic interactions were observed. The possible reasons for the observed magnetic properties in light of their structural analysis will be discussed.

CHAPTER 4. NOVEL MAGNETIC MATERIALS BASED ON ORGANIC RADICALS IN HOST LATTICES

This chapter presents the results of our experimental investigations on establishing novel methodologies to achieve cooperative magnetic interactions between organic spin systems. It is well known that no long range order is possible in a purely one-dimensional system at finite temperatures. The bulk of the investigations in the area of purely organic magnetic materials have been based on one-dimensional models. We envisaged that if organic free/ion radicals could be included in a suitable host lattice that mediates the exchange coupling of the spins, interesting cooperative magnetic interactions may be realized. This would also allow flexibility in choosing the appropriate dimensionality.

One of the best known two-dimensional host lattice is graphite. An important property of graphite is that a wide variety of guests (alkali metals, alkaline earth metals, rare earth metals, halogens, transition metal halides
etc.) can be inserted between the graphene layers, thus forming the well known graphite intercalation compounds (GIC's). We considered the preparation of GIC's having organic radicals as intercalants. It was expected that the spins of the radicals would interact through the mediation of the conduction electrons of graphite, leading to novel magnetic materials. The approach we followed is described in Section 2, and involves the intercalation of a suitable electron donor like an alkali metal into graphite, followed by a strong organic acceptor; the electrons donated to the graphite gallery in the initial step would be subsequently partially or fully transferred to the organic acceptor. The net result is the production of the alkali metal - organic acceptor ion radical salt as an intercalant in graphite. We developed a simple two step procedure to prepare these ternary intercalation compounds using highly oriented pyrolic graphite. They were characterized by weight uptake, infra red spectral and powder diffraction studies. The magnetic properties of these materials were probed with the help of variable temperature esr and SQUID magnetometry. Our studies showed that tetracyanoquinodimethane (TCNQ) does not intercalate, perhaps owing to its size. However intercalation experiments were successful with the smaller tetracyanoethylene (TCNE) molecule producing ternary systems with the first and second stage potassium-GIC's, CgK and C_{24}K respectively. Detailed powder diffraction studies following the 00l peaks indicated that the final products formed with CgK are inhomogeneous mixtures of CgK and KC_{n}(TCNE)_{x}. However, the esr studies revealed that the spin properties of these compounds were very different from the parent CgK, including a Curie - Weiss ferromagnetic coupling in restricted
temperature regions in one of the stoichiometries. On the other hand \( \text{C}_{24}\text{K} \) forms a homogeneous ternary intercalation compound with TCNE. Magnetic susceptibility studies showed a Curie-Weiss behaviour down to 140K with a positive Weiss constant of 29K. Strong antiferromagnetic interactions take over at lower temperatures in all the cases. The interesting ferromagnetic behaviour observed in restricted temperature regimes is novel and warrants further research.

We were interested in investigating the nature of spin interactions of organic radicals between the extreme limits of isolated molecules in solution and the bulk crystalline state. For this purpose we chose polystyrene as a suitable amorphous host which is unlikely to intervene in the spin interactions. We focused our attention on diphenylpicrylhydrazyl (DPPH) a stable free radical, included in polystyrene film. High concentrations of DPPH are required to initiate exchange interactions among radicals in the film; however, conventional film growth techniques did not allow homogeneous inclusion of more than 15 - 20% of DPPH in polystyrene. We developed a simple procedure to make good quality polystyrene films containing appreciable amounts (up to 50%) of DPPH, by casting these films on water surface. These radical doped films were studied using esr spectroscopy. Strong dependence of line widths on the concentration of the radical was noticed. Further, esr signal intensity versus temperature plots indicated fairly strong antiferromagnetic interactions between the spins as opposed to nearly Curie paramagnetic behaviour observed in the crystalline state of DPPH. We discuss possible orientational ordering of the radicals in
the film as a result of the preparation procedure and the likely origin of magnetic exchange interactions in the host lattice.

CHAPTER 5. OVERVIEW OF THE PRESENT WORK AND FUTURE PROSPECTS

This chapter provides a summary of the studies presented in this thesis, with possible avenues for future studies. The results of the semiempirical computational studies on organic conjugated and non-conjugated radicals are summarised. An overview and the relevance of the novel charge transfer complexes, metal coordination compounds and ternary graphite intercalation compounds we have developed in our attempt to design new approaches to molecule-based magnetic materials, is presented. Directions for future work in this area including experimental verification of the mode of spin coupling in nonconjugated multiradicals is provided. Suggestions, both in terms of more extensive experimental and theoretical modelling studies on the novel ternary intercalation compounds we have developed in the present work, are also mentioned.
CHAPTER 1. INTRODUCTION

Section 1, presents an introduction to the phenomenon of magnetism. An overview of the relevance of molecular magnetism in the backdrop of the general field of magnetism is presented in Section 2. The varieties of magnetic order relevant to the present work are also discussed. Various models proposed for achieving ferromagnetic or ferrimagnetic interactions in organic and organometallic systems are summarized in Section 3. Approaches to the design of purely organic ferromagnets are reviewed in detail in the next Section. The final section in this chapter describes the motivation for the present work and the layout of this thesis.

CHAPTER 2. COMPUTATIONAL STUDIES OF SPIN COUPLING IN ORGANIC CONJUGATED AND NONCONJUGATED RADICALS

In connection with the topological models proposed for the design of polymeric organic ferromagnets, several empirical rules have been put forth to predict the ground state spin of organic di and multiradicals. In the introductory Section of this Chapter, we review these rules. We have addressed the problem of spin coupling in organic radicals using semiempirical quantum chemical calculations. The computational methods we have employed are summarised in Section 2.