

ORGANIC RADICALS FOR ELECTRONIC MATERIALS

A Dissertation Presented

by

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To my dear Hakan

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ABSTRACT

ORGANIC RADICALS FOR ELECTRONIC MATERIALS

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Synthesis and magneto-structural characterization of hydrogen-bonded organic nitronyl nitroxide and verdazyl radicals were done. 35diMeO-4OHPhNN displayed 1D antiferromagnetic interactions attributed to the chain contacts between radical NO groups. Benzimidazole-based verdazyl radicals 2BImverd, and 5BImverd did not give diffraction quality crystals and were only characterized by EPR. The analogues 2BImisoverd and 5BImisoverd both gave x-ray diffraction quality single crystals that displayed formation of hydrogen-bonded chains through the imidazole moieties. The magnetic susceptibility results indicated the presence of weak 1D AFM interactions for both radicals. The weakness of interactions was attributed to bulky isopropyl groups pushing the molecules apart and decreasing spin orbital overlap.

A series of organic radical solid solutions (alloys) were made using BImNN and its fluorinated analogue F4BImNN. $(\text{F4BImNN})_x(\text{BImNN})_{(1-x)}$ with $x < 0.8$ gave orthorhombic unit cells, while $x > 0.88$ gave monoclinic unit cells. $(\text{F4BImNN})_x(\text{BImNN})_{(1-x)}$ ($x = 0.1, 0.17, 0.25, 0.5, 0.75, 0.83, 0.9$) displayed ferromagnetic interactions with $J/k = (+)14\text{--}22$ K, mainly controlled by hydrogen-bonded assembly of the radicals. Magnetic analysis over 0.4-300 K showed ordering behavior for

all of these materials. The ordering temperatures of the orthorhombic samples increased linearly as $(1-x)$ increased from 0.25 to 1.00. The variation was attributed to increased inter-chain distance as more F4BImNN was added into the orthorhombic lattice. The monoclinic samples were not part of the same trend, which was attributed to a change in the inter-chain arrangement. This was the very first study giving such complete magnetostructural detail linking ordering behavior to specific crystallographic features and intermolecular contacts.

The magnetic behavior of F4BImNN was investigated at increased external pressures. The crystallographic c -axis (along which hydrogen bonds form) was compressed by 3% at 10 kbar and by 4% at 17.8 kbar. The overall lattice volume contracted by 12% from ambient pressure to 17.8 kbar. The magnetic susceptibility measured over 1.8-300 K showed an increase in ferromagnetic exchange interactions as pressure increased. The increase in exchange strength was attributed to pressure-increased overlap of spin orbitals in the hydrogen-bonded chains, which favored 1-D ferromagnetic interaction.

Electron paramagnetic resonance experiments on a single crystal of F4BImNN were also performed. The variation in g -value as a function of the crystal's position with respect to the applied magnetic field was investigated. The angular dependence of g was more pronounced at temperatures below 30 K.

Pyrrole-based nitronylnitroxide radicals mNNPP, N-PN and 35NNPP were studied. mNNPP displayed formation of 1D chains with weak intra-chain FM interactions, N-PN gave 1D AFM interactions, and 35NNPP showed intramolecular FM and intermolecular AFM interactions.

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CHAPTER 1

INTRODUCTION

Magnets have been known to human kind at least since the discovery of lodestone. According to the legend, about 4000 years ago a Greek shepherd named Magnes observed that the nails on his shoes were attracted by a big black rock, which is called ‘magnetite’ (Fe_3O_4). Later, around 200 B.C. the first floating compass was developed in China. Since then magnetic materials have become crucial to much of the development of science and technology, and thus are crucial for the establishment of our present high-tech society.

Traditional magnets that we use in our daily lives are atom-based and made from inorganic metals in which the electron spins contributing to magnetic ordering are located in d- or f- type orbitals. These electron spins couple with each other through covalent bonds in three dimensions. Molecule-based magnets, however, might have spins on their p- orbitals as well, and their spin sites need not to be covalently bonded to be able to couple with each other. This property brings a lot of flexibility into the design of magnetic materials.

Another advantage of molecule-based magnets is that, due to the rich structure of carbon chemistry, small modifications to a molecule can be tailor-made to craft desired properties such as low density, solubility, mechanical flexibility, transparency, electrical insulation, etc. Furthermore, molecule-based magnets can help combine magnetic ordering with other properties such as photo-responsiveness and biocompatibility.

Considering these facts it is expected that in near future the progress of the research in molecular magnetism will extend itself more and more into innovative technology markets.

Research on stable organic radicals as molecule-based magnets has advanced significantly after the discovery of the first purely organic ferromagnet p-NPNN in 1991 (Figure 1.1).¹ As new organic radicals with ferromagnetic exchange interactions were discovered scientists tried to find crystallographic packing motifs that can help rationalize the exchange interactions between unpaired spins.

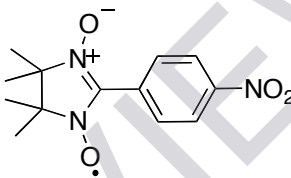


Figure 1.1 Structure of p-NPNN.

One of the potential ways to control crystal packing – and hence magnetism – is through the use of systems that are capable of forming hydrogen bonds. Hydrogen bonding is an excellent way to create self-assembly and (to some extent) control of intermolecular exchange between organic radicals. If one can identify ways to alter the crystal structure of a radical molecule in a desired way by adding/subtracting hydrogen-bonding moieties, then the synthetic chemist can try to design a molecule with the desired magnetic properties. Although complete control of crystal packing remains futuristic, scientists still continue to pursue this possibility.

A big part of this dissertation contains research about the synthesis and magneto-structural characterization of hydrogen-bonded organic radicals. In the past, Sugawara^{2, 3}

and Veciana⁴⁻⁶ groups have worked on attaching hydroxyphenyl and dihydroxyphenyl groups to nitronylnitroxide (NN) moieties, yielding solid-state radicals with spin ordering behaviors. Lahti group have studied sterically hindered *p*-hydroxyphenyl NNs and checked the effects of steric hindrance on crystallography and magnetism of the compounds.⁷ I have worked on a phenolic NN radical, 35diMeO-4OHPhNN (Figure 1.2), which has the potential to form a hydrogen-bonded structure through its phenol group.

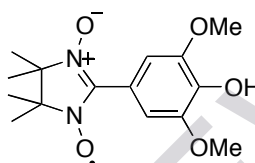


Figure 1.2 Structure of 35diMeO-4OHPhNN.

In the same line of research, I synthesized 2- and 5-benzimidazole substituted oxoverdazyl radicals that are shown in Figure 1.3. Verdazyl radicals are air and moisture stable, and have been studied as molecular magnetic materials. Imidazole is a good scaffold moiety for radical assembly that can form hydrogen-bonded chains through the donor NH group to the acceptor nitrogen in the next molecule. There are already examples of imidazole and benzimidazole substituted nitronylnitroxide radicals in the literature that show the formation of hydrogen-bonded chains.⁸⁻¹⁰ Sizes and the shapes of the verdazyl radical moieties are roughly comparable to those of the NN radical moieties. As a result, based on the sizes of the radicals it seemed likely that these verdazyl radicals could form similar hydrogen-bonded chains to the previously synthesized benzimidazole-based radicals.

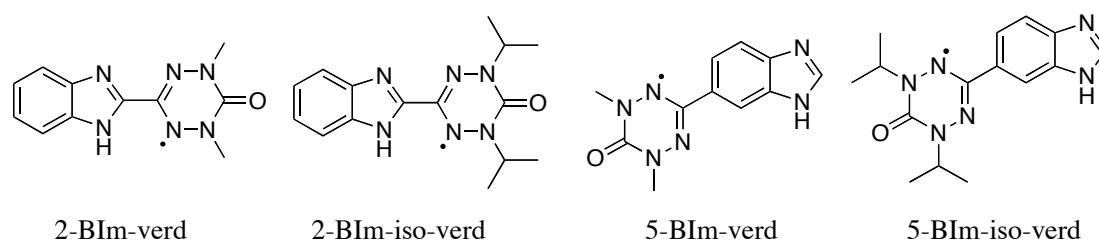


Figure 1.3 Structures of the benzimidazole-based oxoverdazyl radicals.

Another group of molecules that I pursued was pyrrole-substituted NN radicals. These types of radicals were studied by Sugawara¹¹⁻¹³ group as spin polarized donor molecules. For my studies I investigated the magnetic behavior of two new pyrrole-based organic radicals, m-NNPP and 3,5-diNNPP (Figure 1.4). I also looked at the magnetic properties of N-PN, which was previously synthesized by Nakazaki et al.¹¹ but not subjected to magnetic analysis.

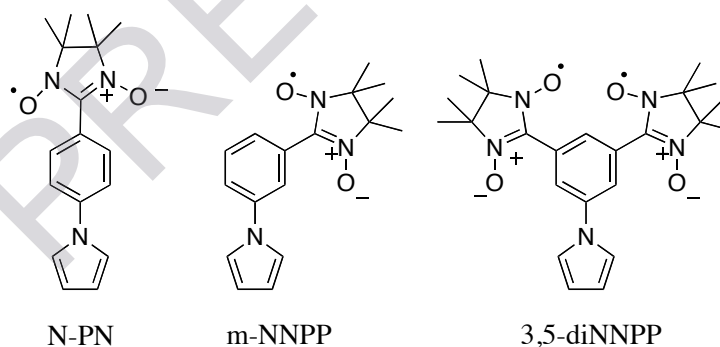


Figure 1.4 Structures of the pyrrole-based nitronyl nitroxide radicals.

Another major topic of interest was organic radical mixtures. Although there has been much effort of trying to manipulate the magnetism of pure organic radicals by tuning the crystal packing of the unit cell, full control is still not possible. Even small

changes on a molecule might end up affecting the magnetic behavior in a non-predictable way. Using radical mixtures with similar crystal packing might be a solution to this problem by providing clearer comparisons between compositionally different materials. In addition, further electronic properties that cannot be seen in single component systems might be achieved through mixtures of crystals and materials. In 2007, Murata et al. used two organic radicals to prepare a solid solution.¹⁴ These radicals, BImNN and F4BImNN, were very similar in structure and volume. Both of them showed dominant one-dimensional ferromagnetic chain exchange through intra-molecular hydrogen bonds. The mixture, (F4BImNN)_{0.5}(BImNN)_{0.5}, showed similarities in terms of magnetism and crystallography to the individual components. With this preliminary information, I have synthesized the previously known organic radical, BImNN^{8, 9}, and its fluorinated analogue, F4BImNN^{10, 15} (Figure 1.5). Using these radicals I prepared a set of organic radical solid mixtures with different compositions, (F4BImNN)_x(BImNN)_{1-x} ($x = 0.1, 0.17, 0.25, 0.75, 0.83, 0.9$), and constructed the phase diagram for crystallography and magnetic behavior for these alloys.

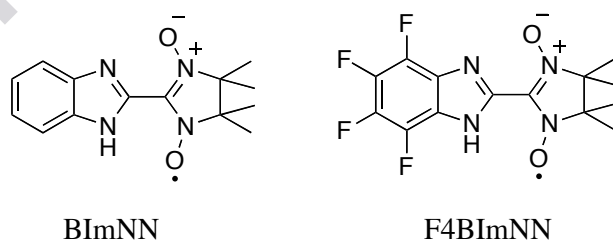


Figure 1.5 Structures of BImNN and F4BImNN

Although mixtures of metal-containing molecular magnets have been studied¹⁶, there are limited examples for purely organic systems. The only related studies for neutral

radicals appear to be those by Mukai et al. on some verdazyl-based alloys.¹⁷⁻¹⁹ Mukai's alloys are based on similar-size co-crystallization; this pioneering work nevertheless lacks full crystallographic details, and do not provide the level of molecular assembly control provided by directional hydrogen-bonding. By comparison, my alloy system was crystallographically fully characterized, proving occurrence of the same hydrogen-bond controlled 1-D chain formation that is seen in the individual component radicals. This was the very first study giving such complete magnetostructural detail linking ordering behavior to specific crystallographic features and intermolecular contacts.

Finally, I investigated the magnetic properties of F4BImNN radical under increased pressure values.²⁰ Investigating the same molecule under different pressures is another way to avoid the complexity of changing the molecular structure while trying to make magneto-structural correlations. Higher pressure can cause changes in the crystallographic packing of a molecule and, as a result, affect the magnetic properties of the material under investigation.^{21, 22} Although organic molecular magnetic solids are excellent soft matter samples for tuning intermolecular interaction effects under pressure, only a limited number of them have been studied under increased pressure.

Detailed descriptions of results from the studies described above are given in subsequent chapters. Some background materials are first introduced in the next chapter to let the reader have an understanding of the basics of magnetism and molecule-based magnets.

Notes

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