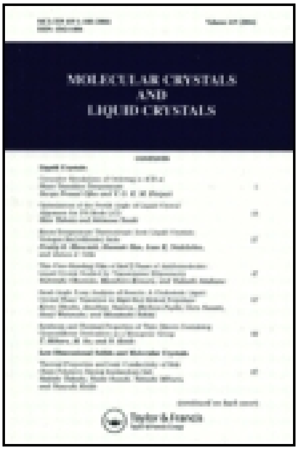

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Polymeric, H-Bonded, and Chelatable Phenoxyl and Nitroxide Radicals

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. Various examples are described of a multi-strategy approach to improvement of multispin exchange design. For example, H-bonded benzimidazole 4-*t*-butylnitroxide shows apparent simple planar 2D-type interaction, with a Weiss constant of $\theta = -4.24$ K and an intraplane exchange interaction of $J = -1.60$ K.

Keywords: hydrogen-bonding; magnetism; phenoxyl; nitroxide; polyradical

INTRODUCTION

A critical part of designing bulk magnetic properties is to control multispin exchange between molecules other multispin arrays. In this paper, we report the synthesis of a number of highly stable organic radicals with H-bonding and chelatable moieties that will be used in constructing supramolecular multispin assemblies. In addition, we use modern organic synthetic strategies to make a regiospecific polyradical with appropriate connectivity for high-spin exchange along one dimension.

1-D EXCHANGE – A REGIOSPECIFIC POLYTHIENYL POLYRADICAL

A much-pursued strategy for organic-based magnetic materials has been the synthesis of polymeric polyradicals. It is important in such polyradicals to avoid spin defects caused by inefficient spin-center generation or connectivity/geometry defects.[1] Pendant-spin polyradicals are not so readily affected by spin defects as are backbone polyradicals, since exchange between pendant sites can in principle bridge a defective monomer, although the magnitude of exchange may be decreased.[2] It has been demonstrated that intrachain ferromagnetic exchange can be achieved for pendant polyradicals with appropriate regioconnectivity, e.g., **1**[3] in Figure 1.

Substantial coplanarity of the pi-network is required for pendant spins to exchange couple.[2] Computations show that a 60 degree torsion of a conjugated backbone can completely isolate pendant spins, explaining why polyphenylacetylene based polyradicals **2** fail to show intramolecular exchange, even when high spin-counts per monomer are achieved.[4] Exchange design strategies to must therefore aim to favor the needed coplanarity.

Cerius^2 force field analysis (Molecular Simulations Inc.,) indicates that regioregular polymer **3** will have modest torsion of the pendant phenyl rings relative to the backbone polythiophene (PT), and that the PT chain itself will be rigidified into a well-conjugated system by the desire of the pendant groups to adopt the alternating anti arrangement shown in Figure 1. AM1-CI computations by our usual methodology[2] indicate that the dimeric intermolecular exchange will be about one kcal/mol in the anti, planar conformation shown. Related polythiophene ethynylene systems have been made,[5] further encouraging extension to a more rigid PT system.

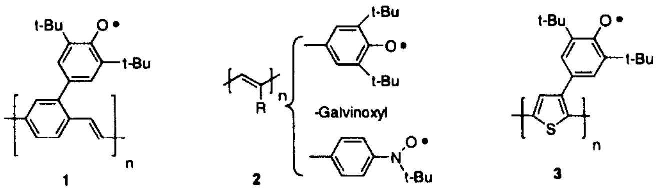


FIGURE 1 Pendant polyradicals with varying exchange coupling.

Figure 2 shows our regiospecific synthesis of polyradical **3**. During our work in this area, Yamamoto and Hayashi described a nonregiospecific synthesis of **3**.[6] We found the Suzuki coupling to be quite effective between the halogenated, protected phenol unit **4** and commercially available (Aldrich) thiophene-3-boronic acid to give monomer **5**. Iodination of **5** was regiospecific to give **6**, which was polymerized to polyether **7** with a degree of polymerization of about six. ^{1}H-NMR spectra showed sharp peaks for **7** with the simplicity of pattern expected for its regiospecific nature.

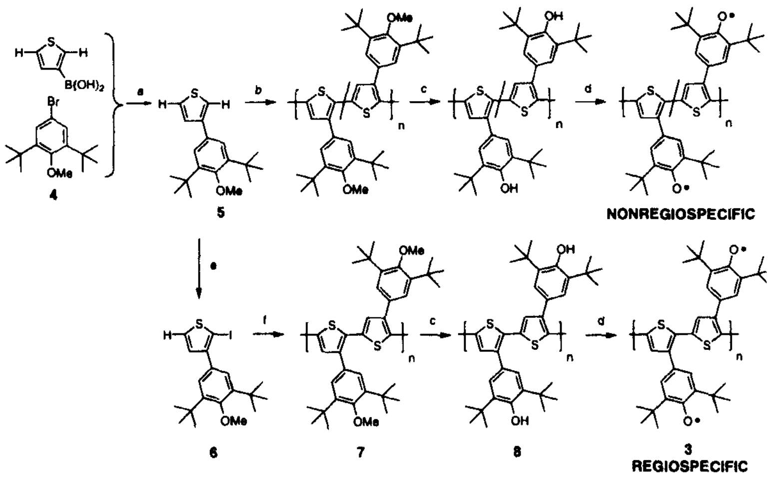


FIGURE 2 Regio- and nonregiospecific polyradical **3**. (a) Pd(PPh$_3$)$_4$,aq Na$_2$CO$_3$,EtOH/PhH,Δ. (b) FeCl$_3$/CHCl$_3$, 3 days. (c) BBr$_3$/CH$_2$Cl$_2$,Δ, (d) PbO$_2$/PhH or PhH/aq KOH-K$_3$Fe(CN)$_6$. (e) I$_2$/HgO/PhH. (f) *n*-BuLi,TMEDA, Δ, CuI.

Prolonged warming of **7** in BBr$_3$/CH$_2$Cl$_2$ led to cleavage of the methyl ether groups and formation of polyphenol **8**, which is readily oxidized in organic solvents to give a deeply colored **3** with a strong, persistent ESR peak at g=2.00464 and UV-vis peaks at 285, 412, 421, 572 nm. It is not straightforward to compare the planarity of nonregiospecific to the regiospecific **3**, but comparison of the UV-vis maximum for nonregiospecific **7** (389 nm, made via iron trichloride oxidative coupling of **5**) to that for the regiospecific material (402, 426 nm) supports a more conjugated structure for the latter. A similar but smaller trend is seen in the photoluminescence spectra, with a 531 nm emission for nonregiospecific **7** vs. 540 nm for regiospecific **7**.

ESR solution spectra of the phenoxyl radical derived from monomer **5** shows observable delocalization of the phenoxyl spin onto the thiophene ring, with hyperfine coupling constants of 1.6 (2H), 3.3, 0.8, and 0.2 G. The large constant resides on the thiophene ring, and corresponds to 10-15% of the spin density, (using McConnell constant Q ~ 30 G).[7] This implies that the polymer backbone of **3** will have sufficient spin density for effective exchange between the pendant groups.

At present we are still seeking to determine the level of intramolecular exchange in regiospecific versus nonregiospecific **3**. The polyradical looses about half of its spin intensity after an hour a room temperature as a solid, but studies such as ESR spin nutation[8] in solution or solid state should be feasible.

CHELATABLE RADICALS FOR SUPRAMOLECULAR ARRAYS

One of the most successful strategies for the design of molecular magnetic materials has been the chelation of stable radicals by paramagnetic ions to give hybrid materials with critical temperatures (T_C) much higher than those of pure organic radicals or polyradicals.[8-10] While a number of such systems have been made, a tremendous variety of combinations remain for testing.

Figure 3 shows chelatable phenoxyl, *t*-butyl nitroxide (tBN), and "benzonitronylnitroxide" (BNN) radicals that we are testing for utility in hybrid radical-metal materials. The first two are well-known radical spin bearing units, but the BNN group has been long overlooked as a possible spin-bearing unit,[11] and only recently has a report appeared[12] confirming the possibilities for isolated stable BNNs as solid materials (BNN, R=Ph). We have found the BNNs to be readily synthesized with various functionality, and that they show solid state stability for weeks under vacuum. All of the systems in Figure 3 were characterized by solution

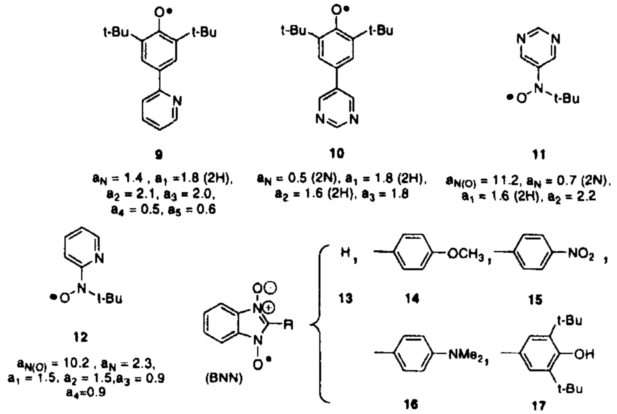
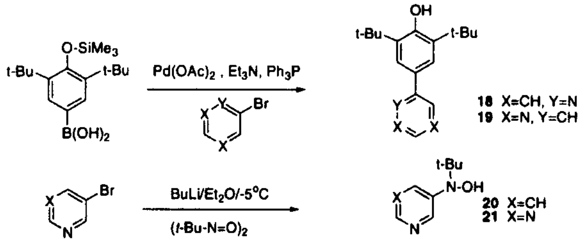


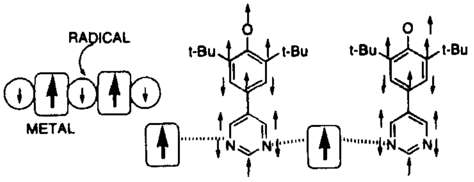
FIGURE 3 Radical building blocks with observed ESR hyperfine coupling (lhfcl) constants in gauss for **9-12**.

ESR spectroscopy to understand their spin density distributions better. The hfc constants obtained in this manner are summarized in Figure 3.

The phenoxyl radicals were generated by lead dioxide oxidation of the phenols **18-19**. The phenolic precursors were synthesized by Suzuki coupling between the appropriate halogenated heterocycle and the trimethylsilyl ether of 2,6-di-t-butylphenol-4-boronic acid. Hydroxylamine precursors **20-21** to tBNs **11-12** were synthesized by typical methods as shown. Compounds **20-21** were somewhat air-sensitive, and had to be converted to the desired radicals by aq sodium periodate oxidation fairly quickly. Autoreduction of the hydroxylamines to *t*-butylamino derivatives occurred readily upon heating. All the radicals of Figure 3 showed high solution stability, and survived solvent removal if inert conditions were used.



The BNNs **13-17** were all synthesized by oxidation of the corresponding 2-substituted-1-hydroxy-3-oxybenzimidazoles – available from *o*-quinone bis-oxime – with lead dioxide or aq sodium periodate to give green-yellow solutions (UV-vis 385, 479 nm for R=Ph) with strong ESR quintuplet spectra due to the presence of two equivalent nitrogen atoms. Typically a_N=4-5 G, a much smaller value than the analogous[13-14] hfc of 7-8 G for tetramethyl-α-nitronylnitroxides, indicating appreciable spin delocalization. Observable delocalization from the nitroxide sites occurs onto the fused benzo-ring, which show a_H~0.3-1.0 G, corresponding to 1-2 % spin density. The ESR results confirm the notion that BNNs should be useful spin-bearing building blocks, at least in terms of spin delocalization and flexibility of synthesis. The BNNs that we have tested to date all show high stability in solution even upon moderate exposure to air, and easily survive removal of the solvent used to generate them from the N-hydroxy precursors, followed by replacement with a different solvent.

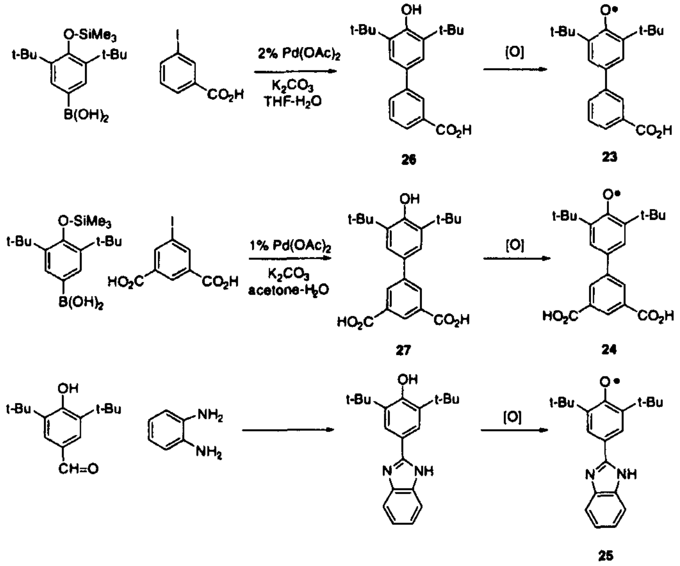


A critical characteristic of a radical unit in a hybrid organic-inorganic array is the spin-density distribution. Ferrimagnetic alignment through antiferro-magnetic exchange between the small spin-density sites of a radical unit and the large moments of paramagnetic metal ions can lead long range alignment of the paramagnetic moments. An example of a favorable spin arrangement using radical **10** as an example is shown above. If such systems can be synthesized, they could have interesting magnetic properties. The nitroxide systems **11** and **12** have typical hyperfine behavior as well as a substantial (presumed positive) spin density $a_N \sim 2$ G *ortho* to the nitroxide, corresponding to a spin density of 7-8%. Their connectivities are such they are potential candidates for overall antiferromagnetic spin pairing with paramagnetic cations. Efforts are underway to generate chelates of **9-12** to test their use in extended molecular solids with effective cation-radical exchange.

H-BONDING RADICALS FOR SUPRAMOLECULAR ARRAYS

Recently, the (4-cyano-2,3,5,6-tetrafluoro-phenyl)dithiadiazolyl radical has been found[16] to order at 36 K, a much higher temperature than that of any other purely organic system to date. This encourages the hope that other such systems can be discovered and designed, if appropriate crystal control motifs can be identified that maximize through-space exchange. H-bonded radicals can yield well-ordered crystals with bulk magnetic ordering.[17-18] Appropriate manipulation of H-bonding motifs could in principle allow molecular design of solid-state packing patterns, hence control of intermolecular exchange interactions.

We are presently engaged in evaluating H-bonding radicals **23-25** for solid state magnetic behavior. The corresponding phenolic precursors **26-27** are high-melting solids that crystallize in the $P\bar{1}$ space group, with **26** showing typical H-bonded pairs, and **27** showing H-bonded chains disrupted by the presence of included solvent molecules (one acetone molecule per phenol molecule). After these phenols are oxidized in the solution phase, they give highly persistent ESR



phenoxyl spectra and show disappearance of the sharp –OH peak at about 3600 cm^{-1} in the FTIR spectrum. We anticipate strong solid-state interactions in these radicals, although their solid state stabilities remain to be quantitatively established.

The phenolic precursor to radical **25** is also quite insoluble in most solvents and has a high melting point. Oxidation with lead dioxide in dimethylsulfoxide yields an indigo blue radical with a strong ESR signal. Addition of water to the oxidation solution precipitates a blue black solid that lacks the phenolic OH stretch at 3600 cm^{-1}. This material has a strong ESR signal at g = 2.0044 in the solid state that is persistent for weeks in air. This material is under study at the present.

Lead dioxide oxidation of the appropriate hydroxylamine precursor **28** gives tBN radical **29** as elementally pure, air-stable, wine-red crystals upon slow evaporation of solvent. Qualitatively, **29** forms 2-D sheets by H-bonding between adjacent stacks of molecules, with a Pbca space group (Figure 4). Stacking occurs along the crystal a-axis, with the sheets forming along the b-axis. Each stack is canted perpendicular relative to its neighboring stack. In a longer range sense, the lattice is centrosymmetric, containing two sets of double-sheets, where each double-

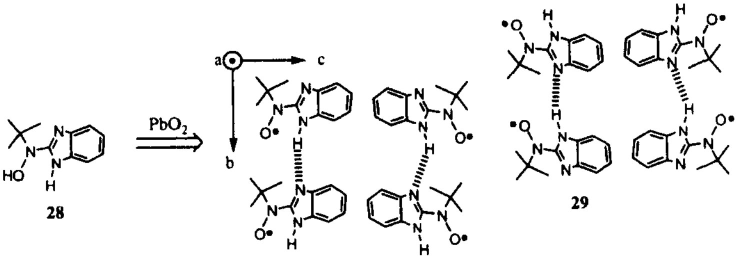


FIGURE 4 Crystal lattice for **29** showing the NH- - -N bonding interaction (dashed lines following the b-axis).

sheet is in turn comprised of a pair of back-to-back H-bonded sheets; the inversion center lies between the double-sheets. All of the nitroxide N-O bonds are aligned syn to . N-H bonds, presumably due to favorable dipolar interactions. The N-H units are H-bonded to imidazole nitrogens in adjacent stacks at a distance of 2.14 Å.

Samples of **29** were subjected to dc and ac magnetic susceptibility analysis down to 1.8 K on a Quantum Design SQUID. After correction for diamagnetic contributions of the sample holder, the susceptibility of the sample was found to follow a Curie-Weiss law at higher temperatures (Figure 5a), with S=1/2, θ = -4.24 K, g=2.029(3), and χ_d =2.81(1)×10^{-4} emu/Oe-mol.

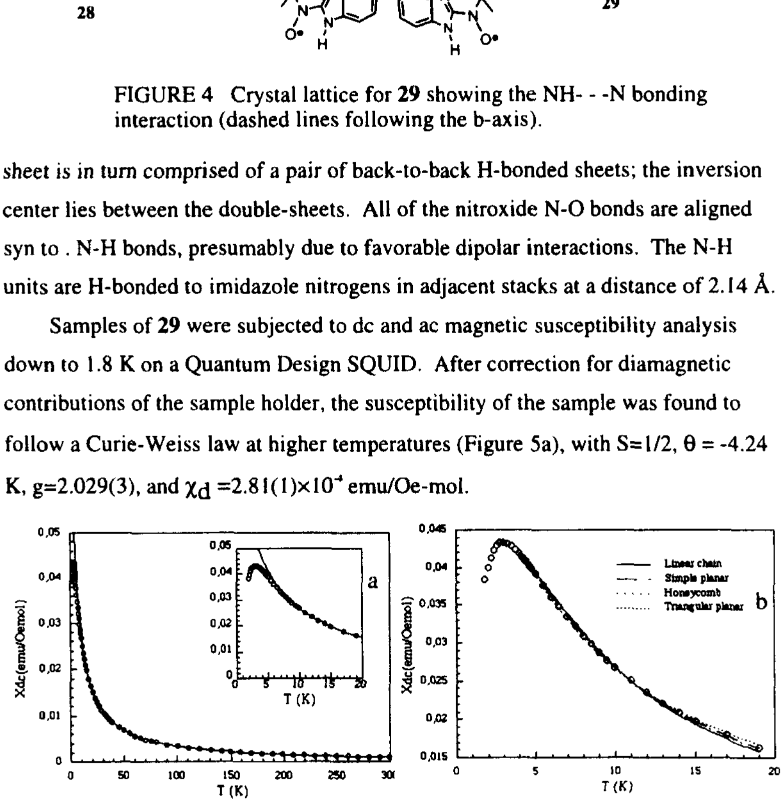


FIGURE 5 (a) Curie-Weiss plot for **29** over 10 - 300 K Insert shows the low temperature region from 1.8-20 K. (b) χ_{dc} versus T(K) for **29** at zero external field. Fitted curves derive from models given in the text.

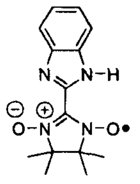
In the low temperature range, the magnetic susceptibility χ(dc) vs T(K) plot shows a broad maximum at about 3 K (Figure 5b). We do not observe a magnetic phase transition at T > 1.8K. slightly below our limit of 1.8 K. We fit the observed data to various low-dimensional Heisenberg S=1/2 models, including a linear chain (Bonner-Fisher curve), simple planar, honeycomb, and triangular planar.

In Table 1, we compare the experimental results with theoretical predictions of the parameter $\tau_m\chi_m$ for different models, using $\tau_m = k_B T_{max} / JS(S+1)$ and $\chi_m = \chi_{max} J / Ng^2(\mu_B)^2$ where χ_{max} is the maximum of the susceptibility and T_{max} is the temperature at that maximum (note that J is actually |J|). The susceptibility behavior of **29** gives a good fit to a simple planar 2D Heisenberg model with S=1/2 spin sites This behavior is quite reasonable when compared to the crystal structure of **29**, which exhibits hydrogen-bonded 2D ordering. If the planar 2D model is assumed with g=2 (appropriate for organic free radicals), we find an intraplane magnetic interaction of J = -1.60 K. Although we have not yet observed the magnetic phase transition for **29** at temperatures down to 1.8 K, the experimental data seems to indicate that the transition temperature is not far from this experimental limit. The overall crystal structure suggests that interactions between the hydrogen-bonded planes should be weak.

TABLE 1. Comparison of $\tau_m\chi_m$ see text definition) for various models

Model	**Theoretical $\tau_m\chi_m$**	**Exptl $\tau_m\chi_m$**
Linear Chain	0.1256	
Simple Planar	0.1170	0.1168*
Honeycomb	0.1093	
Double Layer	0.1293	
Body-center cube	0.1183	
Simple cubic	0.1135	

*if the data is corrected for diamagnetism, $\tau_m\chi_m = 0.1175$.



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The observed behavior for **29** may be compared to that of nitronylnitroxide analog **30**,[19] which crystallizes in the same space group as **25** and has H-bonding between the N-H and nitroxide N-O bonds. However, system **30** shows ferromagnetic coupling in the solid state. Subtle changes in molecular structure can thus yield fairly dramatic changes in bulk magnetic behavior. We continue with attempts to modify systems such as **23-24** and **29** in order to produce self-assembling radicals with strong solid state magnetic exchange interactions.

Acknowledgments

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