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Synthesis of Neutral Spin-Delocalized Electron Acceptors for Multifunctional Materials

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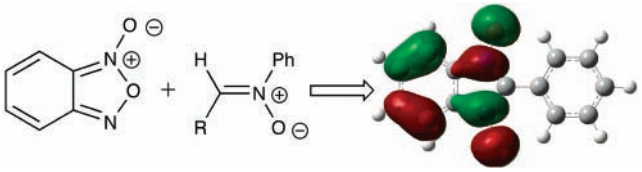
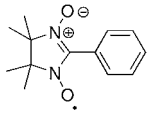
ABSTRACT



A new synthetic route to stable spin-delocalized radicals, annelated nitronyl nitroxides, has been developed on the basis of the condensation of benzofuroxan with aryl nitrones. The electronic structure of the resulting radicals was investigated through absorption spectroscopy, EPR, electrochemistry, and computation (DFT-UB3LYP). The annelated radicals exhibit electronic transitions in the near IR (850–900 nm) and are excellent electron acceptors (E_{red} ~0.0 vs SCE) ideal for the development of multifunctional magnetic materials.

The development of magneto-electronic materials (OMEMs) is central to the emerging field of correlated electronic materials for high-density data storage and quantum computing applications.[1] The dominant strategy involves the incorporation of inorganic spin carriers into semiconducting materials or fabrication of magnetic-semiconducting heterostructures.[2] Recent interest in the development of single-phase processable magneto-electronic materials has led to new developments in organic-based systems that may exhibit slower spin dephasing rates.[3] The development of stable organic radical-based materials with critical conducting or optical properties is a novel strategy toward the discovery of organic magneto-electronic materials.

Stable radicals such as nitronyl nitroxides,[4] thiazyls,[5] and verdazyls[6] play a central role in development of spin-containing materials due to their high stability and ease of synthesis. Annelation of imidazolidinyl-based nitronyl nitroxides (**1**) leads to stable planar spin-delocalized radicals,[7] the benzonitronyl nitronyl nitroxides (BNN 2), which exhibit



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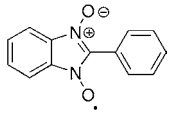

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strong magnetic exchange through efficient $\pi-\pi$ stacking interactions in the solid state.[8] BNN radicals are of interest in that they possess (i) stability toward dimerization in the solid state, (ii) a planar topology for strong intermolecular interactions in the solid state, and (iii) delocalized

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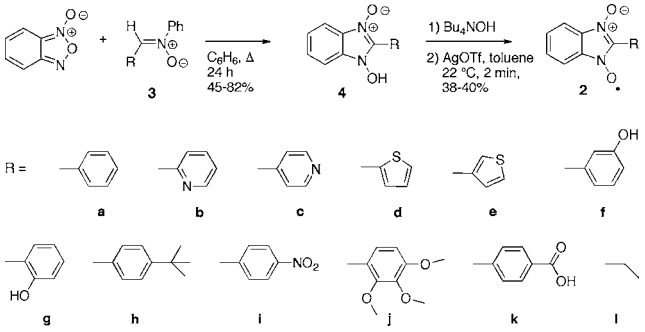
spin density that provides multiple indirect and direct magnetic exchange pathways critical for OMEM development. Relative to other radical classes, investigations into materials incorporating BNN radicals and their electronic structure are sorely missing[8] due to poor yields and low tolerance to diverse functionality associated with existing synthetic routes.

Early synthetic approaches involve the preparation of the radical precursor 1-hydroxy-2-arylbenzimidazole-3-*N*-oxide (**4**) by condensation of nitrosobenzene with benzonitrile oxide,[9] acid-catalyzed condensation of benzo1,2-dioxime with arylaldehydes,[10] and base-catalyzed condensation of primary nitroalkanes.[11] These synthetic routes require either strongly acidic conditions, limiting the nature of the functionality, or suffer from poor reproducibility and low yields. Herein we present a generalized synthetic methodology for annelated nitronyl nitroxides with varying functionality based on the condensation of benzofuroxan with nitrones[12] in nonpolar solvents. The electronic structure of a subset of the resulting radicals was investigated through computation and spectroscopy and found to be give rise to extremely strong electron-acceptor ability with near-IR absorption due to lowering of the SOMO by conjugative effects.

A series of radical precursors were synthesized in which heteroaromatic, aromatic, and alkyl substituents could be incorporated into the C-2 position of the radical (Scheme 1). The functionality of interest can be introduced via an

Scheme 1. Synthetic Pathway to BNN Radicals



aldehyde, which upon condensation with hydroxyl-aminobenzene[13] generates functionalized nitrones[14] in good yield. Condensation of commercially available benzofuroxan with the nitrones of interest in refluxing hydrocarbon solvents cleanly leads to precipitation of the insoluble radical precursors. Thus, the radical precursors can be generated under neutral conditions in high yield. Higher yields of **4** were generally obtained with nitrones containing π-electron-donating groups, perhaps due to increased stability of the nitrone. Oxidation of precursors can be accomplished with lead(IV) oxide or silver(I) triflate in nonpolar solvents to yield yellow-green solutions with EPR spectra characteristic of radicals. Analytically pure samples for investigation can be obtained by flash chromatography to yield green-brown microcrystalline powders (**2a**−**e**, 38−41%). In general the series of radicals are stable in solution and indefinitely in the solid state with the exception of **2b**, **2f**, and **2g**, which were found to decompose in solution within 24 h.

The absorption spectra of radicals **2a**−**e** possess absorptions in the UV region (Figure 1) and a broad weak

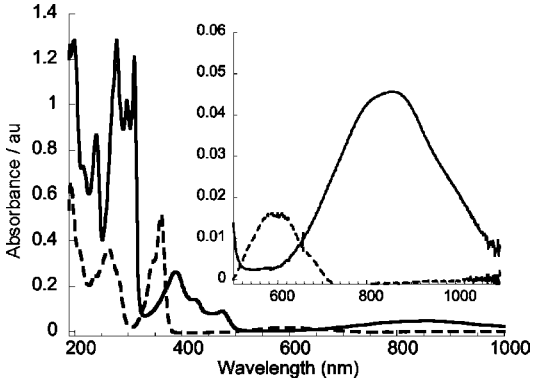


Figure 1. Absorption spectroscopy of 10^{-5} M ACN solutions of nitronyl nitroxide **1a** (- - -) and benzimidazolyl nitronyl nitroxide (BNN) **2a** (—).

absorption band in the near-IR (λ_{max} 825−950 nm, $\epsilon \approx 900$). The energy of the low-energy transition is dependent on the nature of the aryl substituent, lying at higher energy for electron acceptors (825 nm for pyridyl) and lower energy for electron donors (900−925 nm for thienyl) assigned to a symmetry forbidden HOMO−SOMO transition (by TD-DFT computation; see Supporting Information). In contrast, the localized parent imidazolidinyl nitroxide **1** exhibits a diagnostic absorption band in the visible region at 600 nm assigned to a SOMO−LUMO (n−π*) transition.[16]

The EPR spectra of annelated nitronyl nitroxides **2a**−**e** exhibit *g*-values of 2.0070 ± 0.003 and a 5-line pattern with relative intensities of 1:2:3:2:1 consistent with hyperfine coupling to two equivalent nitrogens. Hyperfine coupling constants for the nitrogens in the benzimidazole moiety (N1

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and N3) in **2a**−**e** were found to be $a(N) = 4.328 \pm 0.062$, roughly 60% of that found for the parent radical **1** (7.4 G), consistent with significant spin delocalization into the annelated aromatic moiety. Superhyperfine coupling constants can be resolved for coupling to two equivalent sets of protons on the annelated ring (H_α and H_β) and the aryl substituent protons, consistent with ~10% of the total spin density residing in the annelated ring.

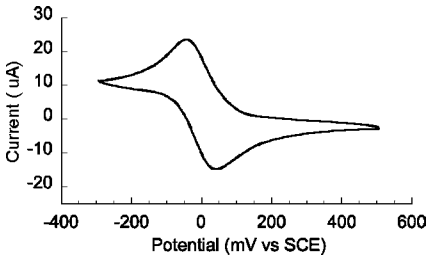

Figure 2. Cyclic voltammetry of the reductive process for a TBAH/ACN solution (50 mV/s) of radical **2a** (—).

The electrochemical behavior of the series of BNN radicals **2a**−**e** was investigated by cyclic voltammetry. The parent radical **2a** exhibits a reversible one-electron reduction at 0.001 V vs SCE ($\Delta E_p = 80$ mV) and an irreversible one-electron oxidation at 1.60 V vs SCE in acetonitrile. Although both the oxidation and reduction processes of pyridyl radicals were found to be irreversible, the reduction potential is decreased relative to the parent **2a** by thienyl subtitution (~0.02 V vs SCE). By comparison, the cyclic voltammogram of radical **1** was found to have an irreversible one-electron reduction at −0.741 V versus SCE and a reversible one-electron oxidation at 1.00 V versus SCE ($\Delta E_p = 90$ mV). The very low reduction potential of BNN radicals indicates that the radical moiety is almost as easily reduced as the standard acceptor compounds TCNE and TCNQ.[17] The strong accepting ability is most likely due to the aromatic 10 π-electron anion formed upon reduction.

Quantum mechanical calculations were carried out at the UB3LYP/6-31G(d,p) level of theory[18] for the series of radicals **2a**−**e**. The optimized geometry for radicals **2a**−**e** indicates geometries in accordance with the expected bond lengths and angles associated with the nitronyl nitroxide and aromatic moieties. Analysis of the SOMO suggests that this orbital is delocalized primarily on the benzimidazole moiety (Figure 3), leading to spin delocalization on the benzimidazole. Little perturbation of the energy of the SOMO is

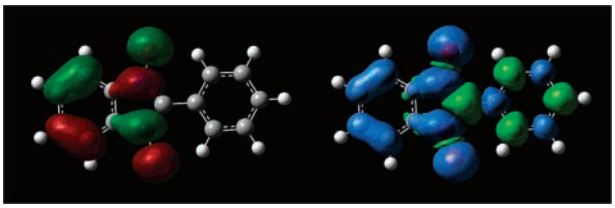

Figure 3. Computational (DFT UB3LYP/6-31G(d,p)) SOMO (left) and SCF spin electron density (right) of **2a** generated with Gaussview03 (isovalue 0.04).

expected with substitution at C-2, consistent with EPR and electronic absorption spectroscopy. In accord, spin densities in the C-2 aryl group are dictated by spin polarization through the nodal C-2 position, consistent with the larger class of nitronyl nitroxides.[19]

Table 1. Spectroscopic Properties of Annelated Radicals

	λ_{max}[a]	a (N1,N3)[b]	a (Hα,Hβ)[b]	$E_{1/2(red)}$[c]	$E_{(SOMO)}$[d]
1	600	7.43		−0.741	0.099
2a	825	4.37	0.93, 0.65	0.001	−0.238
2b	762, 820 (sh)	4.26	0.92, 0.69	~0.2[e]	−0.212
2c	831	4.26	0.91, 0.73	~0.2[e]	−0.225
2d	975	4.37	0.99, 0.74	0.031	−0.216
2e	930	4.38	0.96, 0.69	0.020	−0.216

[a] Acetonitrile solution. [b] EPR hyperfine coupling constants in benzene at 300 K. [c] Values reported vs SCE (solutions measured as 1−5 mM in 0.1 M TBAH ACN vs $Ag/AgNO_3$, Fc/Fc^+ at 50 mV/s). [d] Computational UB3LYP/6-31G(d,p). [e] Irreversible processes, E_p(anodic) values given.

In summary, a robust and versatile synthetic methodology for annelated nitronyl nitroxides has been developed in which a series of heteroaromatic BNN radicals were successfully synthesized. The effect of annelation on the nitronyl nitroxide moiety has been examined spectroscopically and found to be consistent with a lowering of the SOMO energy. The resulting class of radicals possess extremely good electron acceptor ability, long-wavelength absorption spectra, and a spin delocalized electronic structure. This class of planar delocalized radicals provides excellent redox and magnetic properties for the development of multifunctional magnetic materials and is currently under investigation for incorporation into nanoscopic systems.

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Supporting Information Available: Experimental details including syntheses and characterization. This material is available free of charge via the Internet at http://pubs.acs.org.

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