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Strong Ferromagnetic Exchange in 2-(4,5,6,7-Tetrafluorobenzimidazol-2-yl)-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazole-3-oxide-1-oxyl

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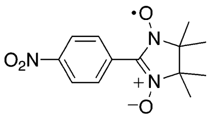
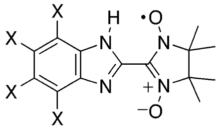
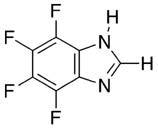
The magnetism of purely organic open-shell molecules has been much-pursued[1] since the discovery that one phase of 2-(*p*-nitrophenyl)-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazole-3-oxide-1-oxyl (pNO2PhNN) is ferromagnetic[2] (FM) at very low temperature. Attempts to increase the magnetic transition temperatures of such molecules require creation or strengthening of reproducible crystal packing motifs that yield extended (beyond dimeric) dimensionalities of exchange interactions. Several radicals show quasi-one-dimensional chain exchange of $\sim$10 K (84 J/mol) or larger.[3] 2-(Benzimidazol-2-yl)-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazole-3-oxide-1-oxyl (BImNN) is a particularly interesting example, forming[3a−c] hydrogen-bonded one-dimensional chains with significant FM exchange. But, this magneto-structural motif can change significantly with even small molecular changes.[4] Because 4,5,6,7-tetrafluorobenzimidazole (F4BIm) exhibits very different crystallography from nonfluorinated benzimidazoles,[5] we synthesized 2-(4,5,6,7-tetrafluorobenzimidazol-2-yl)-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazole-3-oxide-1-oxyl (F4BImNN) to investigate effects of extensive aryl fluorination on the magnetism of the BImNN variants.


pNO2PhNN


BImNN, X = H
F4BImNN, X = F


F4BIm

F4BImNN was made as shown in Scheme 1 and crystallized as blue-black prisms[6] for which room-temperature single-crystal X-ray diffraction shows[7] a monoclinic $P2_1/c$ lattice with intermolecular close contacts as shown in Figure 1. The dihedral angle $\angle$N1−C1−C8−N3 = 22.1(5)° between the benzimidazole unit and the NN ring. Hydrogen-bonded chains along the *c* axis link N1−H in each F4BImNN to O2−N4 of the NN group in a neighboring molecule. The

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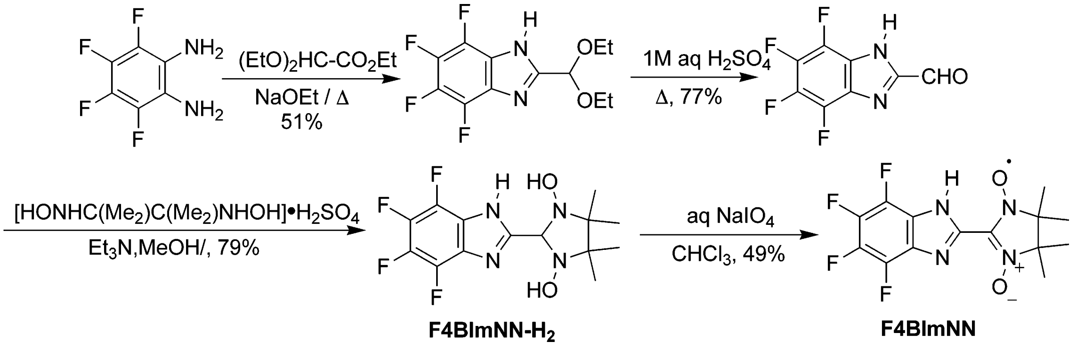
Scheme 1



[N4′]O2′···[H1]N1 and N2′···[H]N(1) distances are 2.814(4) and 3.152(4) Å, and both ∠N1[H]···O2−N4 and ∠N1−H1···N2 contacts are strongly nonlinear, 126.48(19) and 110°, respectively. Although these interactions are not ideal for hydrogen bonding, they are sufficient to organize the F4BImNN molecules into chains.

Yoshioka et al. proposed[3] that FM exchange in BImNN arises from N−O···C close contacts of 3.16 Å with favorable overlap between sites of opposite sign spin density (Figure 1b), so major NO spin densities have the same sign. The corresponding N3−O1···C8′ contacts in F4BImNN are 3.139(4) Å. Computations[8] on a contact dyad of F4BImNN at the crystallographic geometry show FM exchange of 99 J/mol = (+)12 K, in accordance with the qualitative model.

The main crystallographic differences of F4BImNN from BImNN are CF···HC and CF···FC contacts that change the packing of the hydrogen-bonded chains. A set of CF···HC (NN methyl) dipolar contacts in F4BImNN have r{F3···C4} = 3.390(6) Å and r{F1···C6} = 3.162(5) Å and form cyclic tetrads of molecules (Figure 2), each molecule of which participates in a separate hydrogen-bonded chain. The tetrads stack in a highly offset manner, through pairs of aryl CF···FC contacts with r{F1···F2′} = 3.108(4) Å: F1 and F2 are almost vertically stacked (∠C11−F1···F2′ = 86°).

The chains of N3−O1···C8′ contacts in F4BImNN suggest that FM chain exchange interactions can occur. Figure 2 summarizes magnetic studies of polycrystalline F4BImNN. A $1/\chi(T)$ plot (Figure 2a) yields the Curie constant $C = 0.389 \pm 0.001$ emu•K/(Oe•mol) for $T > 40$ K, in accordance with the value of 0.375 expected for $S = 1/2$ units. The Weiss intercept of $\theta = (+)11.0 \pm 0.3$ K shows fairly strong FM exchange.

The $\chi T(T)$ data were analyzed using a literature model[9] for a FM-exchange coupled one-dimensional Heisenberg chain of $S = 1/2$ spin units with a variable exchange constant J/k and a mean field term θ. When a fixed Landé constant of $g = 2.007$ based on electron spin resonance (ESR) measurements of F4BImNN and related NNs is used, the $\chi T(T)$ data at 1000 Oe are well-fit (Figure 2b) using $J/k = (+)17.0 \pm 0.2$ K with a mean field term $\theta = (+)0.44 \pm 0.2$ K. When fixed $g = 2.037$ based on the Curie constant is used, $J/k = (+)16.0 \pm 0.2$ K with a mean field term $\theta =$

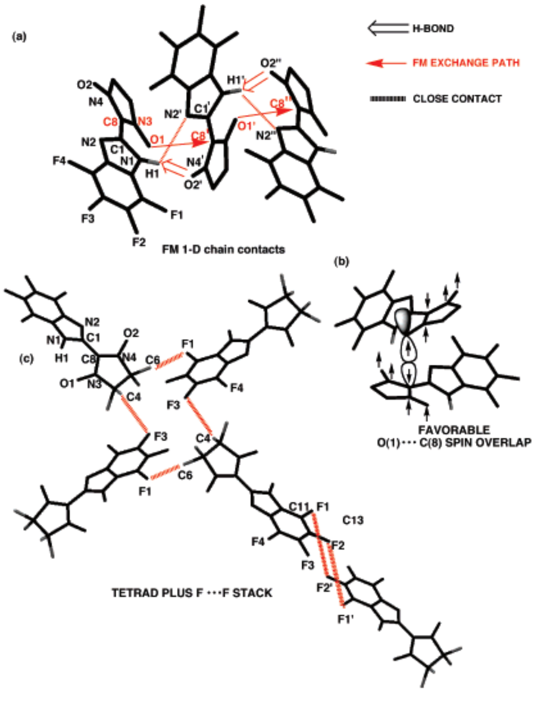


Figure 1. Schematics of F4BImNN crystal packing: (a) intermolecular chain contacts, (b) favorable spin overlap between molecules in the chain, and (c) contacts between molecules in different chains. Methyl groups are omitted in parts a and b for ease of viewing.

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(6) F4BImNN mp = 170−172 °C. ESR (PhMe, 9.7 GHz): 7.22 G (2 N). FTIR (KBr, cm^{-1}): 3396 (NH str). Anal. Calcd for $C_{14}H_{13}F_4N_4O_2$: C, 48.70; H, 3.80; F, 22.01; N, 16.22. Found: C, 49.27; H, 3.99; F, 22.0; N, 15.71. MS (EI): $m/z = 348$.

(7) Crystal data for F4BImNN from chloroform/methanol: Monoclinic, $P2_1c$, $C_{14}H_{13}F_4N_2O_2$, formula weight = 345.28, $T = 293(2)$ K, $Z = 4$, $a = 8.6540(4)$ Å, $b = 20.9710(9)$ Å, $c = 8.8500(4)$ Å, $\beta = 110.297(1)$, $V = 1505.42(12)$ Å^3, D(calcd) = 1.523 g/cm^3, $\mu = 0.138$ mm^{-1}, F(000) = 708, 5128 total reflections, 1783 reflections with $I > 2\sigma$, using 219 parameters, $R_1 = 0.0517$, $wR_2 = 0.1613$; for all data, $R_1 = 0.0863$, $wR_2 = 0.1932$. CCDC #295499.

(8) Computations were carried out using Gaussian 03, at the UB3LYP/6-31G* level for the triplet state and the broken-symmetry UB3LYP/6-31G* level for the singlet state, using crystallographic geometries with C−CH$_3$ replaced by CH groups in the NN moiety. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03*, revision B03; Gaussian, Inc.: Pittsburgh, PA, 2003

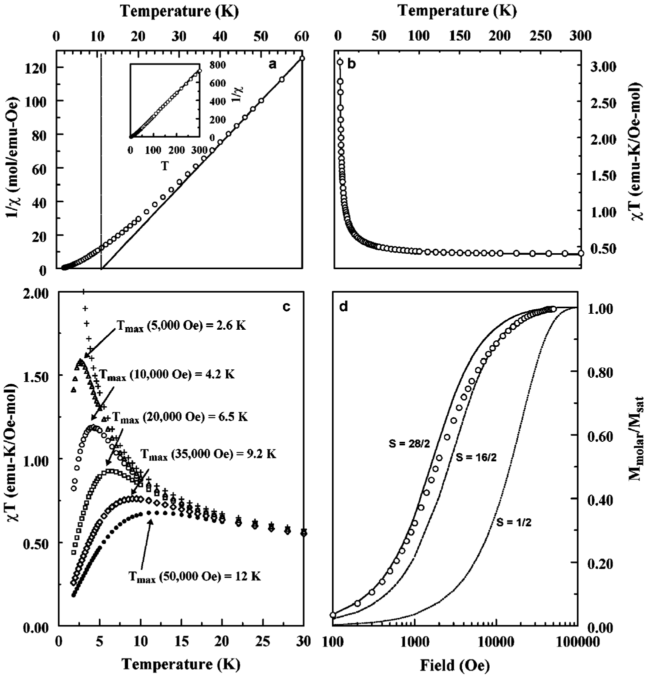

Figure 2. Parts a and b: $1/\chi(T)$ and $\chi T(T)$ plots for F4BImNN at 1000 Oe. Solid lines in part a shows a Curie−Weiss fit to data above 40 K. Solid line in χT vs T is a fit to a one-dimensional FM chain model with $g = 2.007$ (see main text). Part c: $\chi T(T)$ plots for F4BImNN at varying applied fields; the (+) data are from part b. Part d: molar magnetization data for F4BImNN at 1.8 K (circles), showing theoretical Brillouin curves at 1.8 K for $S = 1/2$, 16/2, and 28/2 going from right to left. All susceptibilities corrected for temperature independent magnetism.

(+)0.46 ± 0.2 K. BImNN shows[3] essentially the same exchange constant for $\chi T(T)$ data at 5000 Oe that were fitted at >3 K; these data turn down below 3 K. Figure 2c shows that the $\chi T(T)$ data for F4BImNN also turn down at higher magnetic fields. These downturns come from saturation of the susceptibility. Figure 2d shows the molar magnetization for F4BImNN over 0−50 000 Oe at 1.8 K, normalized against its saturation magnetization of 5400 emu/mol (which is in good agreement with the value of 5585 emu/mol expected for $S = 1/2$ units.) $M_{\mathrm{molar}}/M_{\mathrm{satd}}$ shows a much more rapid increase with field than occurs for typical, nearly isolated $S = 1/2$ units. Comparisons to theoretical Brillouin functions show that the data correspond to an effective spin quantum number in the range $S = 8{-}14$ at 1.8 K. BImNN shows qualitatively similar magnetization behavior corresponding to $S \sim 5$ at 4 K.

The similarity of the exchange behavior of F4BImNN to that of BImNN is interesting because a number of other close variants[4] of BImNN, including different degrees of fluorination and halogenation in varying positions,[10] show significantly different crystallographic and magnetic behavior. The role of heavy fluorination in F4BImNN by comparison to BImNN is not straightforward to interpret. Fluorine can replace hydrogen sizewise, but its high electronegativity seemed likely to produce very different electrostatic interactions for F4BImNN in our initial design planning. A large change in crystallography[5] for F4BIm by comparison to benzimidazole seemed to support the notion that the C−F bonds would strongly influence crystal lattice formation. Perhaps the hydrogen bonding chain motif energetically overrides or complements effects of intermolecular fluoroarene and F···F interactions in F4BImNN. Overall, F4BImNN, like BImNN, forms NO···HN hydrogen bonds and NO···C close contacts that yield an effective FM chain exchange mechanism.

Although the magnetic data at lower field are a good fit to a nearly isolated one-dimensional FM chain model, it is possible that F4BImNN has other exchange interactions that become more manifest at lower temperatures. Further investigations are underway to test this possibility.

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Supporting Information Available: Synthetic details, crystallography, magnetic models used, and density functional theory computations for F4BImNN (PDF), including a crystallographic summary in CIF format. This information is available free of charge via the Internet at http://pubs.acs.org.

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