e) P. G. Gassman, M. R. Callstrom, *J. Am. Chem. Soc.* **1987**, *109*, 7875; f) H. Sinn, W. Kaminsky, H.-J. Vollmer, R. Woldt, *Angew. Chem.* **1980**, *92*, 396; *Angew. Chem. Int. Ed. Engl.* **1980**, *19*, 390; g) R. F. Jordan, *Adv. Organomet. Chem.* **1991**, *32*, 325; h) T. J. Marks, *Acc. Chem. Res.* **1992**, *25*, 57; i) J. J. Eisch, A. M. Piotrowski, S. K. Brownstein, E. J. Gabe, F. L. Lee, *J. Am. Chem. Soc.* **1985**, *107*, 7219; j) R. F. Jordan, C. S. Bajgur, R. Willett, B. Scott, *ibid.* **1986**, *108*, 7410.

[4] For β-methyl and β-alkyl elimination, see a) P. Watson, C. Roe, *J. Am. Chem. Soc.* **1982**, *104*, 6471; b) "Initiation of Polymerisation": P. L. Watson, T. Herskovitz, *ACS Symp. Ser.* **1983**, *212*, 459–479; c) W. Kaminsky, H. Luker, *Makromol. Chem. Rapid Commun.* **1984**, **5**, 225; d) P. L. Watson, G. W. Parshall, *Acc. Res.* **1985**, *18*, 51; e) E. Bunel, B. Burger, J. Bercaw, *J. Am. Chem. Soc.* **1988**, *110*, 976; f) L. Schock, T. J. Marks, *ibid.* **1988**, *110*, 7701; g) B. Burger, M. Thompson, D. Cotter, J. Bercaw, *ibid.* **1990**, *112*, 1566; h) J. Eshuis, Y. Tan, J. Teuben, J. Renkema, *J. Mol. Catal.* **1990**, *62*, 277; i) L. Resconi, F. Piemontesi, G. Franciscono, L. Abis, T. Fiorani, *J. Am. Chem. Soc.* **1992**, *114*, 1025; j) J. J. Eshuis, Y. Y. Tan, A. Meetsma, J. H. Teuben, J. Renkema, G. G. Evens, *Organometallics* **1992**, 11, 362; k) K. McNeill, R. A. Andersen, R. Bergman, *J. Am. Chem. Soc.* **1995**, *117*, 3625; l) A. D. Horton, *Organometallics* **1996**, *15*, 2675; m) L. D'ornelas, S. Reyes, F. Quignard, A. Choplin, J.-M. Basset, *Chem. Lett.* **1993**, 1931.

[5] V. Dufaud, J.-M. Basset (CPE Lyon), XF-B 9508552, **1995**, [*Chem. Abstr.* **1997**, *126*, 293772y].

[6] F. Quignard, C. Lecuyer, C. Bougault, F. Lefevbre, A. Choplin, D. Olivier, J.-M. Basset, *Inorg. Chem.* **1992**, *31*, 928.

[7] a) F. Quignard, A. Choplin, J.-M. Basset, *J. Chem. Soc. Chem. Commun.* **1991**, 1589; b) F. Quignard, C. Lecuyer, A. Choplin, D. Olivier, J.-M. Basset, *J. Mol. Catal.* **1992**, *74*, 353.

[8] J. Corker, F. Lefebvre, C. Lécuyer, V. Dufaud, F. Quignard, A. Choplin, J. Evans, J.-M. Basset, *Science* **1996**, *276*, 966.

[9] S. L. Scott, J.-M. Basset, *J. Mol. Catal.* **1994**, *86*, 5.

[10] Formally, **1** is a $\mathrm{Zr^{IV}}$ $\mathrm{d^0}$ compound with eight electrons if one does not consider the $p_\pi - d_\pi$ interaction between the oxygen lone pair orbitals and the Zr orbitals.

[11] C. Lecuyer, F. Quignard, A. Choplin, D. Olivier, J.-M. Basset, *Angew. Chem.* **1991**, *103*, 1692; *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 1660.

[12] A proposed mechanism[7] includes the following elementary steps: 1) electrophilic activation of a C−H bond of the alkane by a highly electrophilic zirconium hydride on the surface by σ-bond metathesis, 2) β-alkyl migration with formation of an (alkyl)(olefin)zirconium complex, 3) hydrogenolysis of the alkylzirconium complex with liberation of an alkane and formation of a surface (hydride)(olefin)-zirconium complex, 4) insertion by the latter of the coordinated olefin into the Zr−H bond, and 5) hydrogenolysis of the new surface alkylzirconium species to give an alkane with regeneration of the electrophilic zirconium catalyst. No hydrogenolysis was observed with ethane owing to the lack of an alkyl group in the β-position.

[13] For polyethylene and polypropylene IR data, see C. Pouchert in *The Aldrich Library of Infrared Spectra*, **1981**, 3rd. ed.

[14] The polymerization of ethylene or propylene with alumina-supported zirconium hydrides is well known; see, for example, a) A. M. Pyle, K. J. Jens, *J. Mol. Catal.* **1986**, *38*, 337; b) V. A. Zakharov, Y. A. Ryndin, *ibid.* **1989**, *56*, 183; c) J. P. Candlin, H. Thomas, *Adv. Chem. Ser.* **1976**, *132*, 212; d) Y. I. Yermakov, V. A. Zakharov in *Coordination Polymerization* (Ed.: J. C. Chien), Academic Press, New York, **1975**, pp. 91; e) V. A. Zakharov, V. K. Dudchenko, A. I. Minkov, O. N. Efrimov, L. G. Khomyakova, V. P. Babenko, Y. I. Yermakov, *Kinet. Catal.* **1976**, *17*, 643; f) V. A. Zakharov, Y. I. Yermakov, *Catal. Rev. Sci. Eng.* **1979**, *19*, 67; g) L. E. Firment, *J. Catal.* **1983**, *82*, 196; h) P. J. Toscano, T. J. Marks, *J. Am. Chem. Soc.* **1985**, *107*, 653.

[15] S. Reyes, G. P. Niccolai, J.-M. Basset, unpublished results.

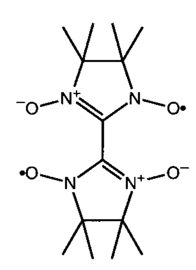
[16] a) D. R. McAlister, D. K. Erwin, J. E. Bercaw, *J. Am. Chem. Soc.* **1978**, *100*, 5966; b) J. E. Bercaw, *Adv. Chem. Ser.* **1978**, *167*, 136; c) M. E. Thompson, S. M. Baxter, A. R. Bulls, B. J. Burger, M. C. Nolan, B. D. Santarsiero, W. P. Schaefer, J. E. Bercaw, *J. Am. Chem. Soc.* **1987**, *109*, 203.

[17] S. A. King, J. Schwartz, *Inorg. Chem.* **1991**, *30*, 3771.

A Spin-Frustrated System Composed of Organic Radicals and Magnetic Metal Ions

Megumi Tanaka, Kenji Matsuda, Tetsuji Itoh, and Hiizu Iwamura*

Antiferromagnetically coupled spins in polynuclear complexes of paramagnetic metal ions[1] and π-cross-conjugated organic polyradicals[2] can be arranged in triangular, "butterfly"-shaped, tetrahedral, or cubane-like structures and combinations of these topologies. Consequently, these materials provide ample opportunities for delineating competing interactions in which two neighboring spins have to align in parallel in spite of the antiferromagnetic coupling. When a degenerate ground state ensues, the system is referred to as spin-frustrated. The versatility of molecule-based magnetic materials will be much enhanced in heterospin systems consisting of paramagnetic metal ions in conjunction with organic free radical bridging ligands.[3] The diradical 2,2′-bis(1-oxyl-3-oxide-4,4,5,5-tetramethyl-imidazolinyl) (bnn), which was first reported by Ullman et al.[4] and later characterized by Rey et al. with respect to its magnetic properties,[5] captured our attention as an interesting bis-bidentate paramagnetic ligand for magnetic metal ions. We report here a new spin-frustrated system consisting of manganese(II) bis(hexafluoroacetylacetonate) ($[\mathrm{Mn(hfac)_2}]$) and bnn with a butterfly spin arrangement.



bnn

Complexation was effected by mixing anhydrous $[\mathrm{Mn(hfac)_2}]$ and bnn. Dark green crystals were obtained, and their composition was found to be 2:1, $[\{\mathrm{Mn(hfac)_2}\}_2(\mathrm{bnn})]$, by elemental analysis.[6] The crystal and molecular structure (Figure 1) was determined by X-ray crystallographic analysis.[7] The molecular structure of bnn in the complex is very similar to that reported for free bnn.[5] The C1−C8 bond length of 1.44(2) Å is almost the same as that in the free ligand (1.439(3) Å), and the dihedral angle between the two "Ullman's nitronyl nitroxide radical" moieties is 55° in the complex as well as in bnn itself. These similarities suggest that the bnn ligand forms the $[\mathrm{Mn(hfac)_2}]$ complex with minimal structural perturbation and that the magnetic interaction between the two radical centers should only be marginally modified by complexation.

Magnetic measurements of $[\{\mathrm{Mn(hfac)_2}\}_2(\mathrm{bnn})]$ were performed on a SQUID susceptometer/magnetometer. The

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[*] Prof. Dr. H. Iwamura, M. Tanaka, Dr. K. Matsuda, Dr. T. Itoh
Institute for Fundamental Research in Organic Chemistry
Kyushu University
6-10-1 Hakozaki, Higashi-ku, Fukuoka, 812-81 (Japan)
Fax: (+81)92-642-2735
E-mail: iwamura@ms.ifoc.kyushu-u.ac.jp

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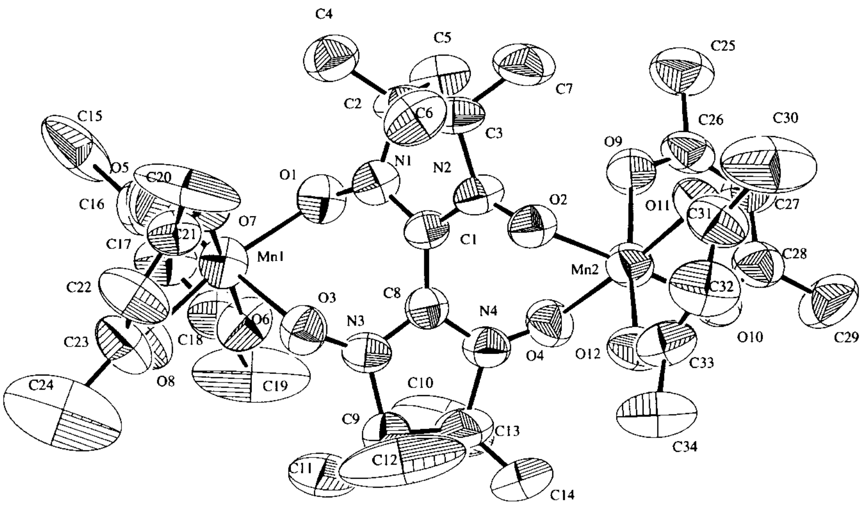


Figure 1. ORTEP drawing of [{Mn(hfac)$_2$}$_2$(bnn)] with thermal ellipsoids at the 50% probability level. The fluorine and hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: C1–C8 1.44(2), Mn1–O1 2.150(8), Mn1–O3 2.201(9), O1–N1 1.28(1), O3–N3 1.28(1), N2–O2 1.28(1), N4–O4 1.25(1), O2–Mn2 2.168(7), O4–Mn2 2.18(1); O3-Mn1-O1 83.8(3), Mn1-O1-N1 126.8(6), N3-O3-Mn1 124.5(6), O2-Mn2-O4 84.8(3), Mn2-O4-N4 127.3(7), N2-O2-Mn2 121.6(6).

temperature dependence of the paramagnetic susceptibility χ at 500 G is presented as a χT vs. T plot in Figure 2. The χT values remained almost constant from 300 to 2 K.

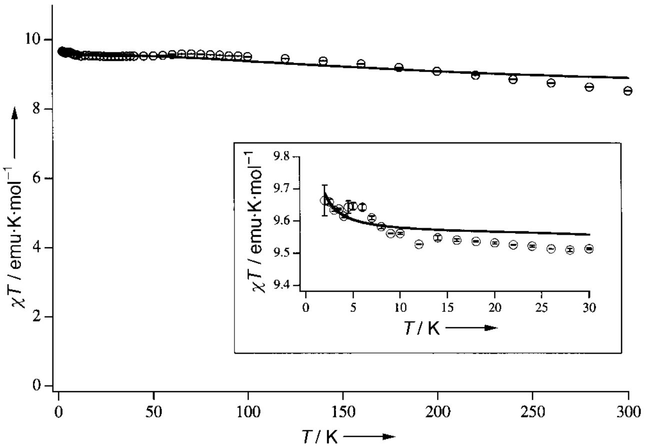


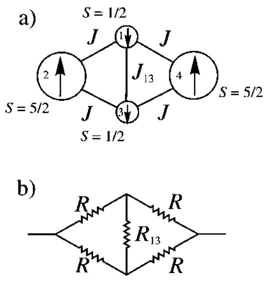
Figure 2. χT vs. T plot for [{Mn(hfac)$_2$}$_2$(bnn)] at 500 G. The solid line represents the theoretical curve (see text).

The spin Hamiltonian $\boldsymbol{H}$ for this butterfly system is given by Equation (1),[1b] where J is the exchange coupling parameter between the 3d spins of Mn^{II} and the 2p spins of the organic ligand (corresponding to the spins of the "wing" and the "body", respectively, of the butterfly), and J_{13} is the interaction between the two 2p spins of the organic ligand (Scheme 1 a). The eigenvalues E are given by Equation (2); $\boldsymbol{S}_T = \boldsymbol{S}_1 + \boldsymbol{S}_2 + \boldsymbol{S}_3 + \boldsymbol{S}_4$, $\boldsymbol{S}_{13} = \boldsymbol{S}_1 + \boldsymbol{S}_3$ and $\boldsymbol{S}_{24} = \boldsymbol{S}_2 + \boldsymbol{S}_4$.

$$\boldsymbol{H} = -2J(\boldsymbol{S}_1 \cdot \boldsymbol{S}_2 + \boldsymbol{S}_2 \cdot \boldsymbol{S}_3 + \boldsymbol{S}_3 \cdot \boldsymbol{S}_4 + \boldsymbol{S}_4 \cdot \boldsymbol{S}_1) - 2J_{13}\boldsymbol{S}_1 \cdot \boldsymbol{S}_3 \qquad (1)$$

$$E = -J[S_T(S_T+1) - S_{13}(S_{13}+1) - S_{24}(S_{24}+1)] - J_{13}[S_{13}(S_{13}+1)] \qquad (2)$$

A theoretical equation was derived for the temperature dependence of χ due to the Boltzmann distribution of the four spins among the energy levels and fitted to the observed data (Figure 2). The best fit provided $J/k_B = -68.1 \pm 4.6$ K and $J_{13}/k_B = -408 \pm 28$ K. The latter is close to that for the free ligand bnn (−447.4 K),[5] and its absolute value is about 10% smaller. Both J and J_{13} are negative, which confirms that any two neighboring spins are antiferromagnetically coupled. Therefore, the four-spin system must have a competing interaction, since two neighboring spins have to align in parallel in spite of the antiferromagnetic coupling.



Scheme 1. a) Spin alignment for the ground state of [{Mn(hfac)$_2$}$_2$(bnn)]; b) Wheatstone bridge.

The field dependence of the magnetization of [{Mn(hfac)$_2$}$_2$(bnn)] was measured at 2 K. The fitting of a theoretical Brillouin function to the observed data (Figure 3) suggests that the populated state is close to the $S = 4$ state (Scheme 1 a). Although J_{13} is more negative than J, the latter wing–body antiferromagnetic interaction appears to dominate, and the two $S = 1/2$ spins of the bnn moiety are obliged to align in parallel. The butterfly configuration and two $S = 5/2$ spins of the manganese ions at the wing sites therefore play an important role in dictating this spin configuration.

Equation (2) reveals that the ground state is $S = 4$ when $6|J| > |J_{13}|$ or degenerate among $S = 0, 1, 2, 3, 4, 4$ and 5 when $6|J| = |J_{13}|$. The present case of $6|J| \approx |J_{13}|$ suggests the latter possibility, that is, a genuine spin-frustrated system.

The butterfly configuration of the four spins (Scheme 1 a) and the ineffectiveness of a large J_{13} interaction in aligning the two body spins in antiparallel in [{Mn(hfac)$_2$}$_2$(bnn)] offer a

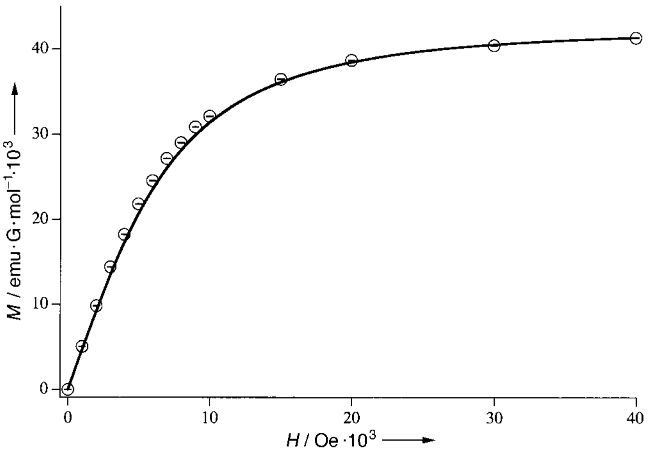


Figure 3. Dependence of the magnetization M of [{Mn(hfac)$_2$}$_2$(bnn)] on the field strength H at 2 K. The solid line indicates the theoretical curve for $S = 4$.

formal comparison of these systems with a Wheatstone bridge in an electric circuit (Scheme 1b). In a balanced Wheatstone bridge, no current flows through R_{13} even if R_{13} is very small. With respect to information processing at the molecular level, the mimicking of an electric circuit by molecular materials is instructive.[8]

We have succeeded in constructing a heterospin system which displays competing interactions between organic radicals and transition metal ions. In this system the large antiferromagnetic interaction was made ineffective by the butterfly spin configuration, and J and J_{13} are sufficiently large to realize the degeneracy of a ground-state spin-frustrated system.

Experimental Section

Preparation of the sample: A suspension of [Mn(hfac)$_2$] · 2H$_2$O (165 mg, 0.32 mmol) in *n*-heptane (40 mL) was heated at reflux to remove H$_2$O by azeotropic distillation. The dark green solution obtained by adding bnn (50 mg, 0.16 mmol) in CH$_2$Cl$_2$ (20 mL) was concentrated on a rotary evaporator to remove CH$_2$Cl$_2$. The green precipitate was collected by filtration to afford dark green plates of [Mn$_2$(hfac)$_4$(bnn)] (153 mg, 76 %). The sample for X-ray crystallography was recrystallized from CH$_2$Cl$_2$/heptane: IR (KBr): $\tilde{\nu} = 1258, 1651, 3002$ cm^{-1}.

Magnetic measurement: A fine-crystalline sample was mounted in a capsule and measured on a Quantum Design MPMS-5S SQUID susceptometer at 500 G. Corrections for the diamagnetic contribution were made with Pascal's constants.

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[1] a) J. Villaian, *J. Phys. C Solid State Phys.* **1977**, *10*, 1717–1734; b) J. B. Vincent, C. Christmas, H.-R. Chang, Q. Li, P. D. W. Boyd, J. C. Huffman, D. N. Hendrickson, G. Christou, *J. Am. Chem. Soc.* **1989**, *111*, 2086–2097; c) J. K. McCusker, J. B. Vincent, E. A. Schmitt, M. L. Mino, K. Shin, D. K. Coggin, P. M. Hagen, J. C. Huffman, G. Christou, D. N. Hendrickson, *ibid.* **1991**, *113*, 3012–3021; d) J. K. McCusker, C. A. Christmas, P. M. Hagen, R. K. Chadha, D. F. Harvey, D. N. Hendrickson, *ibid.* **1991**, *113*, 6114–6124; e) D. N. Hendrickson in *Research Frontiers in Magnetochemistry* (Ed.: C. J. O'Connor), World Scientific, Singapore, **1993**, pp. 87–108; f) O. Kahn, *Molecular Magnetism*, VCH, New York, **1993**, chap. 10.5; g) O. Kahn, *Chem. Phys. Lett.* **1997**, *265*, 109.

[2] a) K. Awaga, T. Okuno, A. Yamaguchi, M. Hasegawa, T. Inabe, Y. Maruyama, N. Wada, *Phys. Rev. B* **1994**, *49*, 3975–3981; b) J. Fujita, M. Tanaka, H. Suemune, N. Koga, K. Matsuda, H. Iwamura, *J. Am. Chem. Soc.* **1996**, *118*, 9347–9351.

[3] a) A. Caneschi, D. Gatteschi, P. Rey, *Prog. Inorg. Chem.* **1991**, *39*, 331–429; b) H. Iwamura, K. Inoue, T. Hayamizu, *Pure Appl. Chem.* **1996**, *68*, 243–252; c) N. Yoshioka, M. Irisawa, Y. Mochizuki, T. Kato, H. Inoue, S. Ohba, *Chem. Lett.* **1997**, 251–252; d) H. Oshio, T. Watanabe, A. Ohto, T. Ito, U. Nagashima, *Angew. Chem.* **1994**, *106*, 691–692; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 670–671; e) D. Luneau, J. Laugier, P. Rey, G. Ulrich, R. Ziessel, P. Legoll, M. Drillon, *J. Chem. Soc. Chem. Commun.* **1994**, 741–742.

[4] E. F. Ullman, D. G. B. Boocock, *J. Chem. Soc. Chem. Commun.* **1969**, 1161–1162.

[5] F. Alies, D. Luneau, J. Laugier, P. Rey, *J. Phys. Chem.* **1993**, *97*, 2922–2925.

[6] Elemental analysis calcd for C$_{34}$H$_{28}$N$_4$O$_{12}$F$_{24}$Mn$_2$: C 32.66, H 2.26, N 4.48; found: C 32.72, H 2.26, N 4.52.

[7] Crystallographic data for [{Mn(hfac)$_2$}$_2$(bnn)]: C$_{34}$H$_{28}$N$_4$O$_{12}$F$_{24}$Mn$_2$, $M_r = 1250.45$, triclinic, space group $P\bar{1}$, $a = 13.305(1)$, $b = 18.617(1)$, $c = 11.0825(6)$ Å, $\alpha = 101.885(5)$, $\beta = 100.968(5)$, $\gamma = 103.359(6)^\circ$, $V = 2530.6(4)$ Å^3, $Z = 2$, $\rho_{\text{calcd}} = 1.641$ g cm^{-3}, $\mu(\text{Cu}_{\text{K}\alpha}) = 54.26$ cm^{-1}. Data were collected on a Rigaku AFC7R diffractometer at 296 K with Cu$_{\text{K}\alpha}$ radiation ($\lambda = 1.54178$ Å). The structure was solved by direct methods and refined to $R = 0.082$, $R_w = 0.079$, for 3677 unique reflections with $|F_o| > 1.5\sigma(|F_o|)$ and 685 parameters. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-100688. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

[8] a) A. Aviram, *J. Am. Chem. Soc.* **1988**, *110*, 5687–5692; b) A. P. deSilva, H. Q. N. Gunaratne, C. P. McCoy, *Nature* **1993**, *364*, 42–44; c) A. Credi, V. Balzani, S. J. Langford, J. F. Stoddart *J. Am. Chem. Soc.* **1997**, *119*, 2679–2681.

Silanediols: A New Class of Potent Protease Inhibitors[**]

Scott McN. Sieburth,* Thomas Nittoli,
Alfred M. Mutahi, and Luxuan Guo

Lower dialkylsilanediols, with their proclivity for self-condensation [Eq. (1)], are the cornerstone of the siloxane (silicone) industry, and siloxane polymers **2** have a reputation as stable and inert materials.[1] Dimethylsilanediol (**1**) is the best known siloxane monomer and the most prone to polymerization. In contrast, more sterically hindered silane-

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[*] Prof. S. McN. Sieburth, Dr. T. Nittoli, Dr. A. M. Mutahi, L. Guo
Department of Chemistry
State University of New York at Stony Brook
Stony Brook, NY 11794-3400 (USA)
Fax: (+1)516-632-8882
E-mail: ssieburth@ccmail.sunysb.edu

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