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Organic-based Magnets: New Chemistry Physics and Materials for This Millennium

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Organic-based Magnets:
New Chemistry Physics and Materials for This Millennium

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Organic-based materials exhibiting the technologically important property of bulk magnetism have been pioneered in our laboratory and studied in collaboration with many research groups worldwide. These magnets are prepared via conventional organic synthetic chemistry methodologies, but unlike classical inorganic-based magnets do not require high-temperature metallurgical processing. Furthermore, these magnets are frequently soluble in conventional organic solvents and have saturation magnetizations more than twice that of iron metal on a mole basis, as well as in some cases coercive fields exceeding that of all commercial magnets (*e.g.,* Co_5Sm). Also several magnets with critical temperatures (T_c) exceeding room temperature have been prepared. In addition to an overview of magnetic behavior, numerous examples of structurally characterized magnets made from molecules will be presented. Four examples magnetically order above room temperature and as high at 127 °C. These will include $[M^{III}(C_5Me_5)_2][A]$, $[Mn^{III}(porphyrin)][A]$ (A = cyanocarbon etc. electron acceptors) as well as $M[TCNE]_x$ (TCNE = tetracyanoethylene), which for M = V is a room temperature magnet that can be fabricated as a thin film magnet via Chemical Vapor Deposition (CVD) techniques. A newer class of magnets of $[Ru_2(O_2CR)_4]_3[M(CN)_6]$ (M = Cr, Fe; R = Me, *t*-Bu) composition will also discussed. For R = Me an interpenetrating, cubic (3-D) lattice forms and the magnet exhibits anomalous hysteresis, saturation magnetization, out-of-phase, $\chi''(T)$, AC susceptibility, and zero field cooled-field cooled temperature-dependent magnetization data. This is in contrast to R = *t*-Bu, which forms a layered (2-D) lattice. Additionally, new magnets possessing the nominal Prussian blue composition, $M'[M(CN)_6]_x$ and $(Cation)_yM'[M(CN)_6]$, but not their structure, will be described. This forms a series of cation-adaptive structures with $[NEt_4]_2Mn_3(CN)_8$, $[NEt_4]Mn_3(CN)_7$, $[NMeEt_3]_2Mn_5(CN)_{12}$ and $[NMe_4]_3Mn_5(CN)_{13}$ stoichiometries that order as antiferromagnets or ferrimagnets. Finally, Li[TCNE] magnetically orders as a weak ferromagnet (= canted antiferromagnet) below 21.0 K. The structure, determined *ab initio* from synchrotron powder X-ray diffraction data, consists of a planar μ_4-$[TCNE]^{\bullet-}$ bound to four tetrahedral Li^+ ions with two interpenetrating diamondoid sublattices, with closest inter-lattice separations of 3.43 and 3.48 Å. At 5 K this magnetic state is characterized by a coercivity of ~30 Oe, 10 emuOe/mol remnant magnetization, and a canting angle of 0.5°. The structure, DC magnetization at ambient and applied pressure, as well as the AC susceptibility at ambient pressure in addition to the computational analysis of the magnetic couplings will be presented. New physics observed from examples of organic-based magnet will be discussed.

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EDUCATION

Postdoctoral Fellowship	Stanford University	Date	1971- 1972
Degree	Ph.D.	Degree	Bachelor of Science in Chemistry
University	University of California, Los Angeles (UCLA)	University	Wayne State University
Major	Inorganic Chemistry	Major/Minor	Chemistry/Mathematics
Date	June, 1971	Date	March, 1967

PROFESSIONAL EXPERIENCE

Distinguished Professor, Department of Chemistry, University of Utah, Salt Lake City, UT (2001 -)
Adjunct Professor of Materials Science and Engineering, University of Utah, Salt Lake City, UT (July, 1994 -)
Adjunct Professor of Physics and Astronomy, University of Utah, Salt Lake City, UT (July, 2013 -)
Specially Appointed Guest Professor (Full time), Osaka University, Osaka, Japan (Nov - Dec, 2017; Aug - Dec, 2018)
Visiting Professorship, Shanghai University, Department of Chemistry, Shanghai, China (2016)
Lady Davis Visiting Professor, Institute of Chemistry, Hebrew University, Jerusalem, Israel (Dec, 2014 - Apr, 2015)
Visiting Professor, Organic Chemistry Department, Weizmann Institute of Science, Rehovot, Israel (Oct-Dec, 2012)
Schulich Visiting Professorship, Technion, Haifa, Israel, March-April, 2011.
Visiting Professor, Noyori Materials Science Laboratory at Nagoya University (2011-2012)
Professor of Chemistry, University of Utah, Salt Lake City, UT (March, 1993 - 2001)
Professeur Invité, Institut de Science et d'Ingénierie Supramoléculaires (ISIS), Université Louis Pasteur, Strasbourg, France (March, 2005)
Visiting Professor, University of Barcelona, Barcelona, Spain (Spring, 2004; Spring 2005)
Wilhelm Manchot Research Professor, Technische Universität Munich, Garching, Germany (December, 1996)
Visiting Professor, Johannes-Gutenberg University, Mainz, Germany (October, 1996)
Visiting Professor, Structural Chemistry Department, Weizmann Institute of Science, Rehovot, Israel (April-May, 1996)
Research Supervisor for Solid State (Electronic Materials) Chemistry and Physics, Advanced Materials Sciences Laboratory (1986 - 1993) Research Scientist, Central Research & Development Dept., Du Pont Co. (1983 - 1986)
Visiting Professor of Chemistry, Institut de Chemie Moleculaire, Universite de Paris-Sud, Orsay, France (July, 1991)
Visiting Scientist, Structural Chemistry Department, Weizmann Institute of Science, Rehovot, Israel (June-July, 1985)
Visiting Professor of Chemistry, University of Pennsylvania, Philadelphia, PA (January, 1988 - May 1988)
Manager of Energy Research, Occidental Research Corporation, Irvine, CA (June, 1983 - September, 1983)
Principal Research Scientist and Group Leader of the Organometallic Group (March, 1979 - June, 1983)
Visiting Professor of Chemistry, University of California, Irvine, CA (January, 1981 - March 1981)
Project Manager and Member of Technical Staff, Rockwell International Science Center, Thousand Oaks, CA (March, 1978 - March, 1979)
Scientist, Physical and Chemical Sciences Laboratory, Webster Research Center, Xerox Corporation, Webster, NY (August, 1973 - March, 1978) Associate Scientist, Chemistry Research Laboratory, Rochester Corporate Research Center, Xerox Corporation, Webster, NY (August, 1972 - August, 1973)

AWARDS

International:
American Physical Society's *James C. McGroddy Prize for New Materials* (2007)
American Chemical Society Award for *Chemistry of Materials* (2000)
Center of Excellence (CoE) Visiting Professor, Nagoya University (2004)
Japan Society for the Promotion of Science Fellow (2000)
Pinguin Foundation's Wilhelm Manchot Research Professorship, Technische Universität Munich, Garching, Germany (1996)

State:
Governor's Medal for Science and Technology, State of Utah (2004)
Utah Award from the Central Utah and Salt Lake City Sections of the American Chemical Society (2003)

University:
University of Utah's Distinguished 2001 Research/Creative Award
Research Identified as being in the "Top 10 Great Research Ideas from the University of Utah" (Fall 2004 issue of *Continuum*).
Wayne State University, The Distinguished Alumni Award (1998)
Phi Lambda Upsilon (PLU) Award for Excellence in Undergraduate Research for developing a computer program to determine the composition of an inorganic coordination complex
National Science Foundation (NSF) Undergraduate Research Fellowship.

PATENTS (6)

Joel S. Miller has 6 patents that include an optical toner fusing system, ink jet fabrication of printed circuit boards, and glass coating compositions. The latter two have been commercialized. In addition, he has a patent on the deposition of thin film room organic magnets, as well as two on new materials, a strong electron acceptor (cyanil).

AUTHOR PROFILE

Joel S. Miller's profile has been published: *Angew. Chem. Int. Ed.* **2013**, *52*, 10688–10689:
https://onlinelibrary.wiley.com/doi/pdf/10.1002/anie.201305568

PUBLICATIONS (>550)

Joel S. Miller has authored >575 publications covering his investigations in solid state materials with magnetic, electrical, and optical, properties as well as synthetic, structural, and the photochemistry of 1,2-dithiolene complexes, reactions of coordinated isocyanides, dinitrogen, and carbon monoxide ligands, and in the development and understanding of catalysts and of 'metal-like' and ferromagnetic molecule-based inorganic, organic, and polymeric compounds. His primary current research interests include the development and exploitation of molecule-based magnets as well as the surface modification of materials to impart specific properties, as well as extraordinary long (~2.9 Å) multicenter C-C bonds, and unusual electron transfer reactions such as reduction of a ligand upon an overall oxidation.

HGHLY CITED RESEARCHER

Joel S. Miller has been selected as an ISIHighlyCited Materials Scientist, Thomson Scientific
h-factor: 79 (excluding books edited) [+ one patent (147 citations)]

BOOKS EDITED and AUTHORED (19)

Synthesis and Properties of Low-Dimensional Materials, J. S. Miller and A. J. Epstein, eds., Annals of the New York Academy of Sciences, Vol. 313 (1978), ISBN-0-89072-069-X (939 p).

Extended Linear Chain Compounds, J. S. Miller, ed., Plenum Publishing Corporation, Vol. 1 (April, 1982), ISBN-0-306-40711-6 (481 p).

Extended Linear Chain Compounds, J. S. Miller, ed., Plenum Publishing Corporation, Vol. 2 (March,1982), ISBN-3-306-40712-4 (517 p).

Extended Linear Chain Compounds, J. S. Miller, ed., Plenum Publishing Corporation, Vol. 3 (January,1983), ISBN-0-306-40941-0 (561 p).

Chemically Modified Surfaces in Catalysis and Electrocatalysis, J. S. Miller, ed., *A. C. S. Symposia Series,* Volume 192 (July, 1982), ISBN-0-8412-07 27-5 (301 p).

Ferromagnetic and High Spin Organic Materials, J. S. Miller and D. A. Dougherty, Guest Eds., *Molecular Crystals, Liquid Crystals*, Volume 176 (Nov., 1989), ISBN-2-88124-402-5 (562 p).

Molecular Magnetic Materials, O. Kahn, D. Gatteschi, J. S. Miller, and F. Palacio, Eds. *NATO Advanced Research Workshop,* Vol. E198, Kluwer Academic Publishers (May, 1991), ISBN-0-7923-1243-0 (411 p).

Chemistry and Physics of Molecular-Based Magnetic Materials, H. Iwamura and J. S. Miller, Guest Eds., *Molecular Crystals, Liquid Crystals*, Vol. 232/233 (1993), ISSN-1058-725X (726 p).

Molecule-Based Magnetic Materials, J. S. Miller and Arthur J. Epstein, Guest Eds., *Molecular Crystals, Liquid Crystals*, Volume 271-274 (1995), ISSN-1058-725X (882 p).

Molecular Magnetism: From Molecular Assemblies to the Devices, E. Coronado, P. Delhaès, D. Gatteschi, and J. S. Miller, eds. *NATO Advanced Studies Workshop,* Volume E321, Kluwer Academic Publishers (1996), ISBN-0-7923-4130-9 (590 p).

Molecular-Based Magnets, K. Itoh, J. S. Miller, and T. Takui, Guest Editors, *Molecular Crystals, Liquid Crystals*, Vol. 305-306 (1997), ISSN-1058-725X (1113 pages).

Molecule-based Magnets, *Mat. Res. Soc.* Thematic Issue, J. S. Miller, A. J. Epstein, Guest Editors, Nov. 2000

Magnetism: Molecules to Materials, J. S. Miller, M. Drillon, eds. Wiley-VCH (2001), ISBN 3-527-29772-3 (437 p)

Magnetism: Molecules to Materials II, J. S. Miller, M. Drillon, eds. Wiley-VCH (2001), ISBN 3-527-30301-4 (498 p)

Magnetism: Molecules to Materials III, J. S. Miller, M. Drillon, eds. Wiley-VCH (2001), ISBN 3-527-30302-2 (388 p)

Magnetism: Molecules to Materials IV, J. S. Miller, M. Drillon, eds. Wiley-VCH (2003), ISBN 3-527-30429-0 (485 p)

Magnetism: Molecules to Materials V, J. S. Miller, M. Drillon, eds. Wiley-VCH (2005), ISBN: 3-527-30665-X (400 p)

Frontiers in Crystalline Matter: From Discovery to Technology, Committee for an Assessment of and Outlook for New Materials Synthesis and Crystal Growth Board on Physics and Astronomy Division on Engineering and Physical Sciences, National Research Council, The National Academies Press (2009), ISBN: 13: 978- 0-309-13800-0 (175 p).

Spin in Organics: A World Scientific Reference, J. S. Miller, ed., World Scientific Publishing Co. Pte. Ltd, 2018, ISBN: 978-981-3228-96-2 (352 p)

PRESENTATIONS

Joel S. Miller has presented well over 600 external presentations at either professional society meetings or academic, industrial, or governmental research centers. Invited lectures have been presented throughout the U.S., Europe, Japan, Korea, USSR, Israel, India, and Australia. A summary list of places where invited seminars have been presented is attached.

CONFERENCES AND SYMPOSIA

Chairmanship (Relevant to Award Nomination) (7 total)

Contemporary Aspects of Chemical Bonding (Divisions of Inorganic and Organic Chemistry of the American Chemical Society, National Meeting, New York, NY, 2003

PROFESSIONAL ACTIVITIES (Abbreviated)

J. Polymer Science, Chemistry Edition ,Advisory Board, 1986 - 1988
Inorganic Syntheses Corporation, 1988 -
Research News Reporter for Molecular Materials, *Advanced Materials*
Chemistry of Materials, Advisory Board, 1990 - 1995
Journal of Materials Chemistry, International Advisory Board and Regional Editor, 1990 - 2003
Advanced Materials, International Advisory Board, 1994 -
Crystal Engineering, International Advisory Board, 1998 -1999
CrystEngComm (Royal Society of Chemistry) Editorial Board, 1999 - 2004; International Advisory Board, 2005-11
Inorganic Chemistry, Editorial Advisory Board, 2001-2003
Chemistry - A European Journal, Editorial Advisory Board, 2000-