

# Joel S. Miller 教授講演会 (アメリカ ユタ大学、特別教授) “Molecule-based magnets designer”

Date and time: 23<sup>rd</sup>, July, 15:00

Room: E211



Joel S. Miller 教授は分子磁性研究の創始者であり、牽引者かつオピニオンリーダーです。1987 年世界で初めての分子磁性体の合成 (1) は、世界中で注目されました。その後、室温以上の分子磁性体 (2)、多重機能性分子磁性体 (3) など、世界トップの成果を発表しています。論文数、引用回数、ともに世界でトップクラス (4) です。Joel S. Miller 教授によって合成された磁性体は実に様々です。室温強磁性体、光応答性磁性体、磁場応答性磁性体、スピングラス、傾角反強磁性体、超硬磁性体などが有名です。彼自身が分子磁性体の歴史と言って過言ではありません。世界トップ研究者の話が聞ける貴重な機会ですので、ぜひお集まりいただき、なぜ彼が分野を作れたか？アイデアはどのようにして生まれてきたのか？得るものは多いと思われます。

1. MILLER, JS; CALABRESE, JC; ROMMELMANN, H; et al., JOURNAL OF THE AMERICAN CHEMICAL SOCIETY, 109, pp769-781, FEB 4 1987
2. “A ROOM-TEMPERATURE MOLECULAR ORGANIC BASED MAGNET”, MANRIQUEZ, JM; YEE, GT; MCLEAN, RS; et al., SCIENCE, 252, 1415-1417, JUN 7 1991.
3. “ORGANIC AND ORGANOMETALLIC MOLECULAR MAGNETIC-MATERIALS - DESIGNER MAGNETS”, MILLER, JS; EPSTEIN, AJ, ANGEWANDTE CHEMIE-INTERNATIONAL EDITION IN ENGLISH, 33, pp385-415, MAR 3 1994.
4. 分子磁性研究の世界トップ研究者には、フランス・ソルボンヌ大学・Michel Verdaguer 教授、フランス・ソルボンヌ大学・故 Olivier Kahn 教授、スペイン・ザラゴザ大学・Fernando Palacio 名誉教授、イタリア フローレンス大学・Dante Gatteschi 教授がいます。
5. HP : <https://chem.utah.edu/directory/miller/>

# 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<sub>5</sub>Sm). 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  $[M^{III}(C_5Me_5)_2][A]$ ,  $[Mn^{III}(\text{porphyrin})][A]$  ( $A$  = 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  $[Ru_2(O_2CR)_4]_3[M(CN)_6]$  ( $M = Cr, Fe$ ;  $R = Me, t\text{-}Bu$ ) composition will also be 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  $R = t\text{-}Bu$ , which forms a layered (2-D) lattice. Additionally, new magnets possessing the nominal Prussian blue composition,  $M'[M(CN)_6]_x$  and  $(\text{Cation})_yM'[M(CN)_6]$ , 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  $\mu_4$ -[TCNE] $^{2-}$  bound to four tetrahedral  $\text{Li}^+$  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  $\sim 30$  Oe, 10 emuOe/mol remnant magnetization, and a canting angle of  $0.5^\circ$ . 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.