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Magnets Based upon the Molecular Solid State

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MAGNETS BASED UPON THE MOLECULAR SOLID STATE

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Abstract A few molecular solids comprised of radicals crystallize in such a manner that the spins ferromagnetically couple. In a rare cases ferromagnetic coupling can lead to ferromagnetic ordering and the formation of a bulk magnet. This occurs below a critical temperature, T_c. Several examples of molecular solid-based magnets have been prepared with T_c's exceeding room temperature. This short review summarizes some of these molecular solid-based magnets prepared in our laboratories.

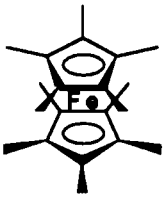
Magnets comprised of components that form molecular or organic solids have been studied for the past decade.[1-6] Unlike classical metallurgically-prepared magnets molecular-solid based magnets are prepared from solution and should enable the alteration of the magnetic properties by organic-synthesis methodologies and enable the combination of magnetic properties with other physical properties while also enabling low-temperature fabrication methods.

In this short review several examples of magnets prepared at room temperature from molecular precursors will be described. This is not meant to be a comprehensive review and the reader is directed existing reviews[1-5] should further details be sought.

The first and best characterized molecular solid-based magnet exhibiting magnetic hysteresis was the electron transfer salt formed from the reaction of decamethylferrocene, $Fe^{II}(C_5Me_5)_2$, $FeCp^*_2$, **1**, with the tetracyanoethylene, TCNE, **2**, leading to $[Fe^{III}(C_5Me_5)_2]^{\cdot+}[TCNE]^{\cdot-}$.[7,8] {This is in contrast, to the reaction of the ferrocene,

$Fe^{II}(C_5H_5)_2$, $FeCp_2$, with TCNE which leads to the formation of diamagnetic $[Fe^{II}(C_5H_5)_2][TCNE]$.}

$[Fe^{III}(C_5Me_5)_2]^{\cdot+}[TCNE]^{\cdot-}$ has an alternating $\cdots D^{\cdot+}A^{\cdot-}D^{\cdot+}A^{\cdot-}\cdots$ crystal structure, Figure 1, and a 4.8 K Curie temperature .[8,9] The observed 16,300 emuG/mol saturation magnetization, M_s, is in excellent agreement with the calculated value of 16,700 emuG/mol for single crystals aligned parallel to the chain axis,[8] and is 36% greater than iron metal on either a per mole or a per iron basis. Hysteresis loops with a coercive field of 1 kOe is observed at 2 K.[8]



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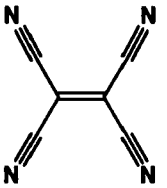

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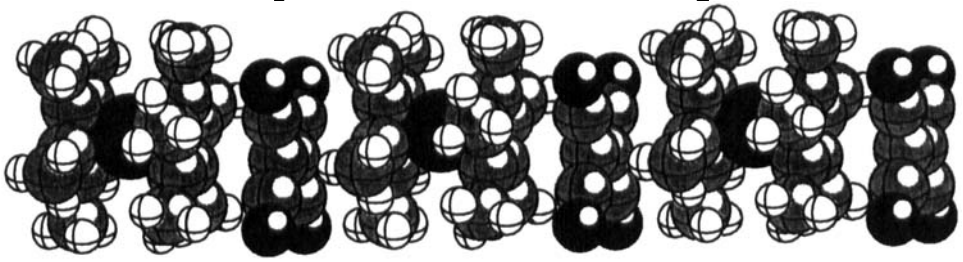


Figure 1. Alternating $\cdots D^{\cdot+}A^{\cdot-}D^{\cdot+}A^{\cdot-}\cdots$ structure observed for $[Fe^{III}(C_5Me_5)_2]^{\cdot+}[TCNE]^{\cdot-}$.[7]

Diamagnetic $[Co^{III}(C_5Me_5)_2]^+$ forms $[Co^{III}(C_5Me_5)_2]^+[TCNE]^{\cdot-}$ which exhibits Curie behavior (θ = -1.0 K).[7] Likewise, diamagnetic $[[C_3(CN)_5]^-$ forms $[Fe^{III}(C_5Me_5)_2]^{\cdot+}[C_3(CN)_5]^-$ which also exhibits Curie behavior (θ = -1.2 K).[7] Thus both the cation and anion must be radicals to stabilize ferromagnetic ordering.

$[M^{III}(C_5Me_5)_2]^{\cdot+}[TCNE]^{\cdot-}$ (M = Mn[10] and Cr[11]) also exhibit cooperative ferromagnetic properties, Figure 2. Additionally, the $[TCNQ]^{\cdot-}$ salts $[M^{III}(C_5Me_5)_2]^+[TCNQ]^{\cdot-}$ (M = Fe,[12] Mn,[13] and Cr[14]) are also ferromagnetic with T_c's reduce from that observed for the $[TCNE]^{\cdot-}$, but follow the same trend. For M = Fe^{III}

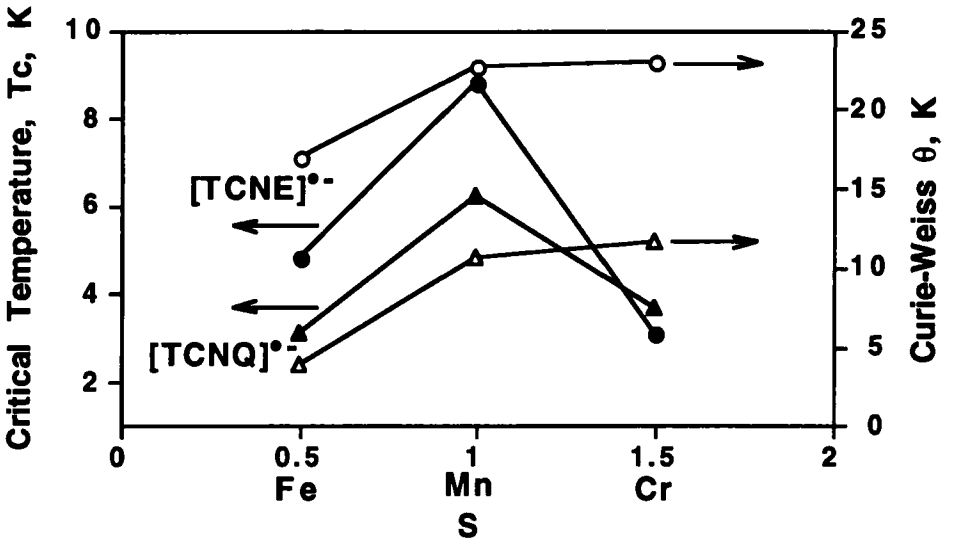


Figure 2. T_c and θ-values as a function of M for $[M^{III}(C_5Me_5)_2]^+[TCNE]^{\cdot-}$ and $[M^{III}(C_5Me_5)_2]^+[TCNQ]^{\cdot-}$ (M = Fe, Cr, Mn).

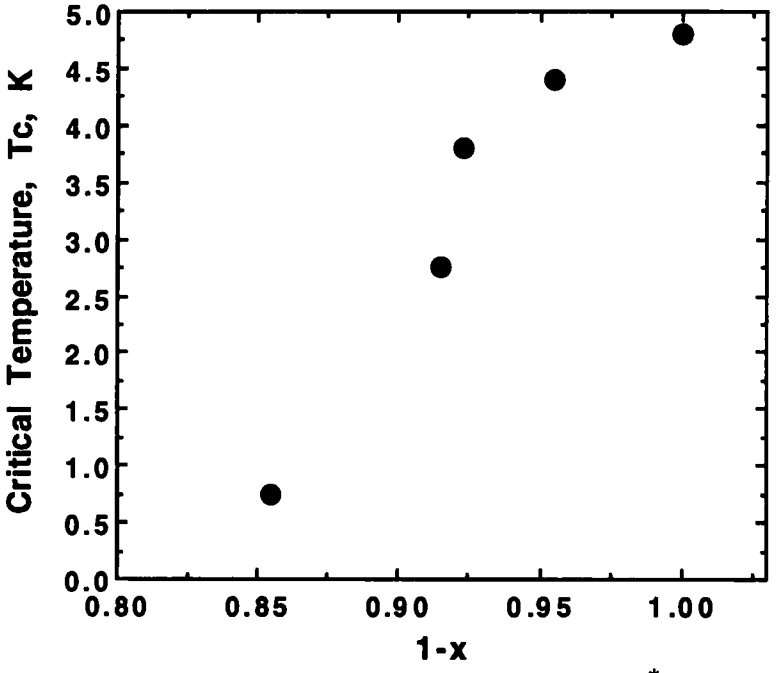
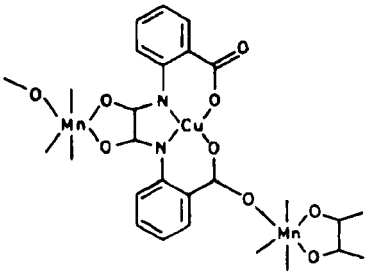


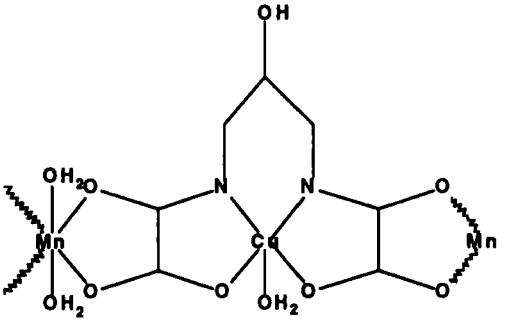
Figure 3. Reduction of T_c as a function of the amount of $[CoCp^*_2]^+$ introduced into the $[FeCp^*_2]^{\cdot+}[TCNE]^{\cdot-}$ structure.

Three phases of $[M^{III}(C_5Me_5)_2]^+[TCNQ]^{\cdot-}$ have been isolated exhibiting para-,[15,16] meta-,[15,17] and ferromagnetic behaviors.[12]

The removal of spins leads to the dramatic reduction of T_c.[18] A 14.5% replacement of spinless Co^{III} for Fe^{III}, reduces the T_c by 84% to 0.75 K from 4.8 K.

Olivier Kahn and his group have reported several examples of ferrimagnets including $Cu^{II}Mn^{II}(obbz)\cdot H_2O$,[19] **3**, with a 14 K T_c. They have also structurally characterized $Mn^{II}Cu^{II}(pbaOH)\cdot 3H_2O$, **4**, which has a T_c of 4.6 K[20] and on loss of water the T_c is increased to 30 K.[21]

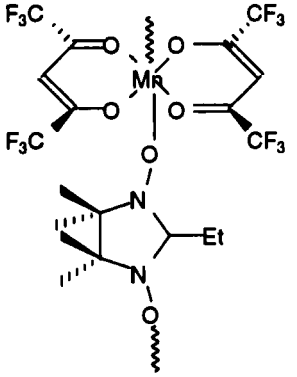




3, $Cu^{II}Mn^{II}(obbz)\cdot H_2O$ **4**, $Cu^{II}Mn^{II}(pbaOH)\cdot 3H_2O$

obbz = oxamidobis(benzoato) pbaOH = 2-hydroxy-1,2-propanediylbis(oxamato)

The collaboration of Dante Gatteschi and Paul Rey developed several Mn^{II}/nitroxide systems including **5** a ferrimagnet with a 8.1 K T_c.[22]



5, $Mn^{II}(hfac)_2NITEt$

hfac = hexafluoroacetylacetonate; NITEt = ethyl nitronyl nitroxide

Since Mn(II) is isoelectronic with V(0) and $[Mn^{III}Cp^*_2]^+[TCNE]^{\cdot -}$ is a ferromagnetic below 8.8 K, we identified the preparation of $[V^I(C_6H_6)_2]^+[TCNE]^{\cdot -}$ as a goal. The reaction of $V(C_6H_6)_2$· and TCNE in dichloromethane, however, lead to a black solid of nominal $V(TCNE)_x{\cdot}y(CH_2Cl_2)$ composition.[23-25] This material is a magnet at room temperature, Figure 4, and is the first example of molecular/organic based material with a critical temperature above room temperature. The critical temperature exceeds room temperature and the thermal decomposition temperature of the sample.

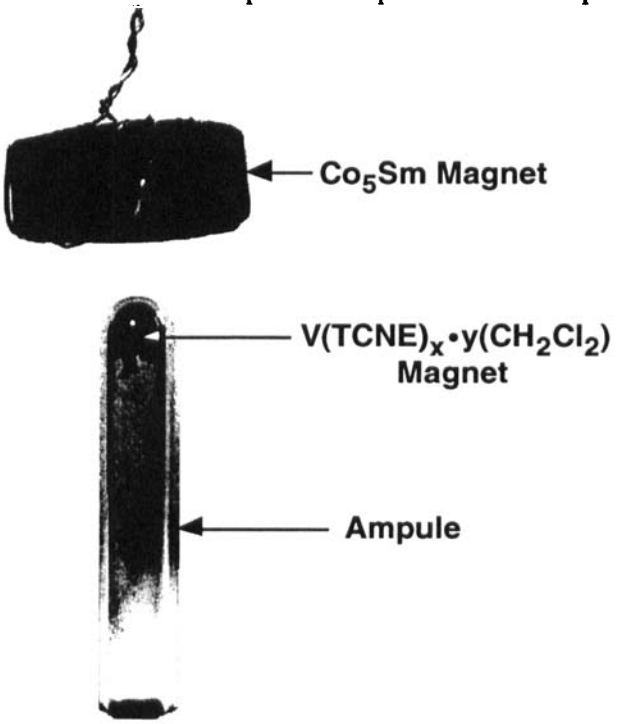


Figure 4. Photograph of a powdered sample of the for $V(TCNE)_x{\cdot}y(CH_2Cl_2)$ magnet being attracted to a magnet.

Metallomacrocycles-based magnets have also been prepared. The first and best characterized example is $[MnTPP]^+[TCNE]^{\cdot -}{\cdot}2$toluene (TPP = *meso*-tetraphenylporphinato) crystallizes as parallel covalently bound $\cdots D^+A^{\cdot -}D^+A^{\cdot -}\cdots$ chains with the $[TCNE]^{\cdot -}$ binding to two $[MnTPP]^+$'s, **6**, in a *trans*-μ_2-*N*-σ-bound manner,[26] Figure 5, and differs from the noncovalently bound $\cdots D^+A^{\cdot -}D^+A^{\cdot -}\cdots$ chains observed for $[FeCp^*_2]^+[TCNE]^{\cdot -}$, Figure 1.

In contrast to $[MnTPP]^+[TCNE]^{\cdot-}$, $[MnOEP]^+[TCNE]^{\cdot-}$ (OEP = octaethylporphine, **7**) exhibits weak ferromagnetic coupling.[27] This weak ferromagnetic coupling is attributed to the lack of a uniform chain, Figure 6. Consistent with this is $[MnOEP][C_4(CN)_6]$ which has strong magnetic coupling and an uniform chain,[27] Figure 7.

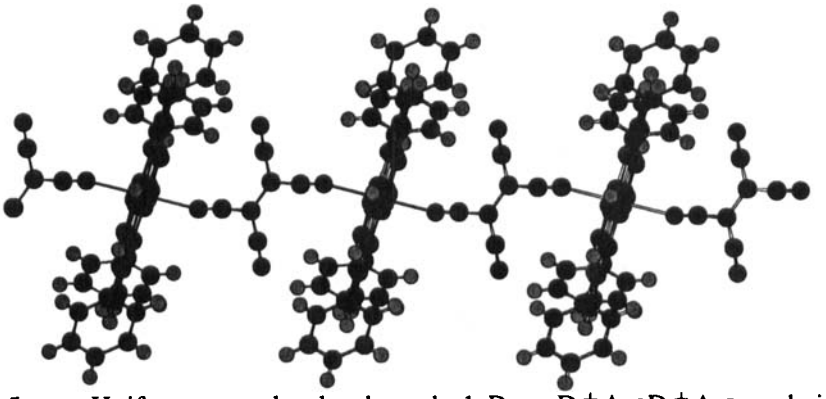
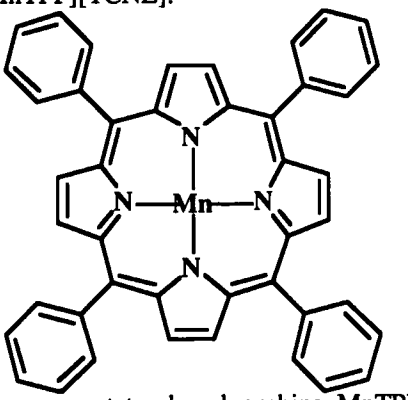
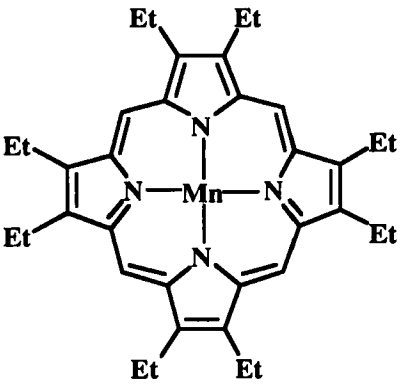


Figure 5. Uniform covalently bound 1-D $\cdots D^+A^{\cdot-}D^+A^{\cdot-}\cdots$ chain of [MnTPP][TCNE].



Manganese tetraphenylporphine, MnTPP, **6**



Manganese octaethylporphine, MnOEP, **7**

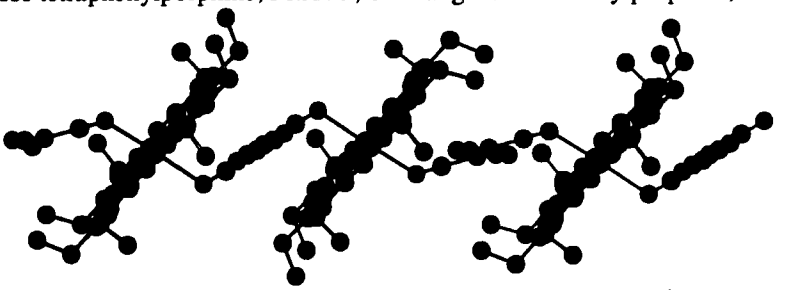


Figure 6. Nonuniform covalently bound 1-D $\cdots D^+A^{\cdot-}D^+A^{\cdot-}\cdots$ chain of [MnOEP][TCNE].

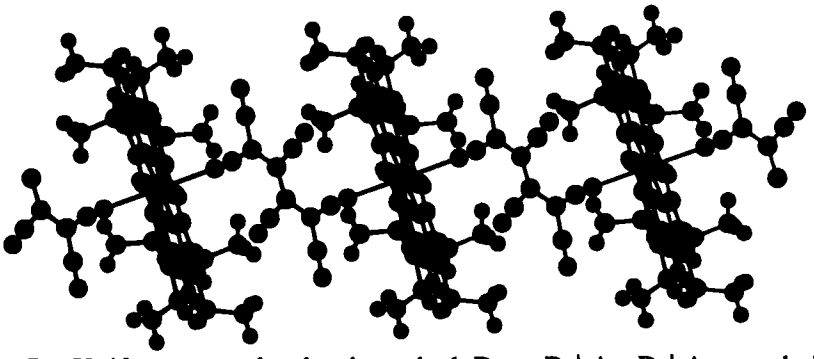


Figure 7. Uniform covalently bound 1-D $\cdots D^{+}A^{\cdot-}D^{+}A^{\cdot-}\cdots$ chain of $[MnOEP][C_4(CN)_6]$.

The study of molecular solid based ferromagnets is a growing arena of study worldwide. The characterization of $[Fe(C_5Me_5)_2]^{\cdot+}[TCNE]^{\cdot-}$ demonstrates that ferromagnetism is achievable in organic-based molecular systems. The time dependence of the increases in T_C for molecular solid-based magnets as compared to that of the organic and ceramic superconductors in illustrated in Figure 8 and magnets with a T_C above room temperature has been achieved. Given the current fast growth of this field it is clear that major advances will be occurring over the next decade in this new multidisciplinary branch of solid state science

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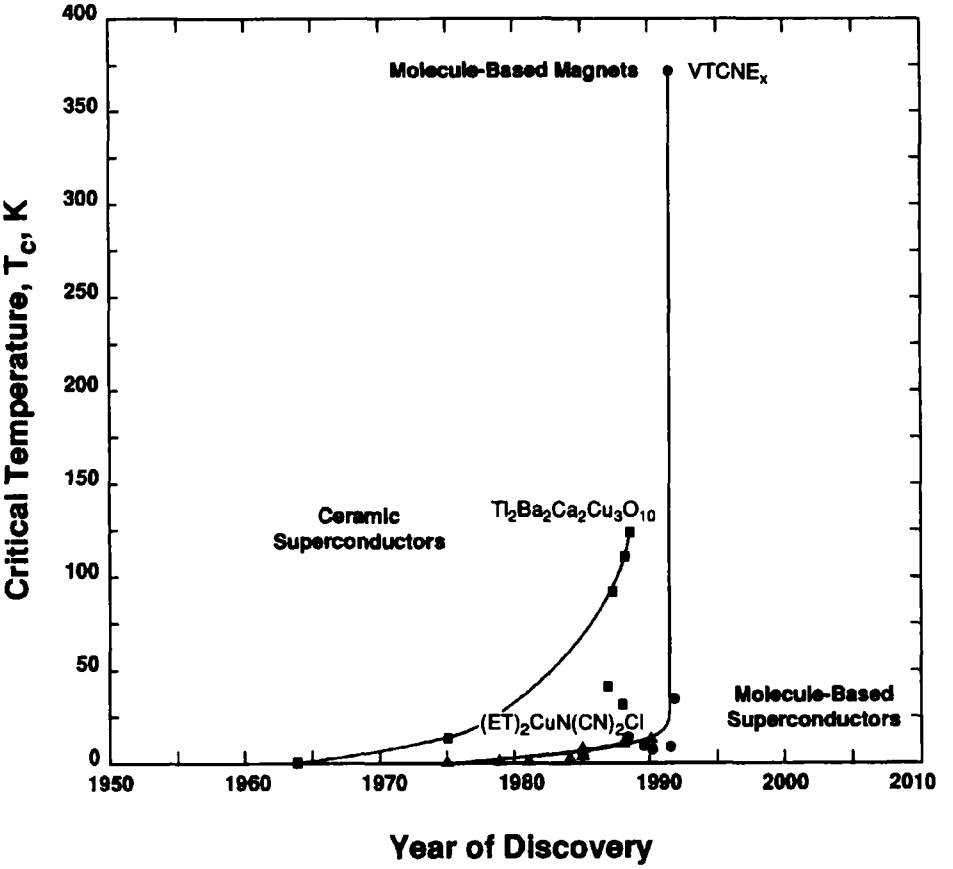

Figure 8. T_c as a function of year of discovery for ceramic superconductors, molecule-based superconductors, and molecule-based magnets.

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