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A Review of Room-Temperature Organic and Molecular Magnets

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Abstract:- Organic and molecular magnets that demonstrate magnetism at ambient temperature are becoming widely popular among researchers. Organic molecules and rare-earth ions, or coordination complexes are used to make these magnets. Molecular and organic magnets have a range of benefits versus atom-based magnets. In many disciplines, a breakthrough in the production of effective room-temperature molecular magnets would be a big advantage. This review article highlights different researchers' successful fabrication of molecule-based and organic magnets with magnetic ordering at ambient temperature. Several aspects of their practical and theoretical approach to magnet synthesis are reviewed. The critical temperature of 1,3,5-triazine-linked porous organic radical framework magnets was 465 K, which is the maximum among all the discussed magnets. This new category of magnets is a fascinating study topic with the opportunity to become a viable solution in the coming years.

Keywords:- *Organic Magnets; Molecule-Based Magnets; Magnetism; Ambient Temperature Synthesis; TCNE.*

I. INTRODUCTION

The molecule-based or molecular magnets are a class of non-traditional magnets formed using organic molecules, rare-earth ions, or coordination complexes [1, 2]. These magnets have p-orbital spin sites. Molecular magnets possess many advantages over traditional metal-based magnets, such as low density, comparatively low-temperature synthesis, easy manufacturing process, and the use of materials abundant in the Earth's crust. Photo-induced magnetism (PIM) is another interesting ability seen in organic magnets. Pejaković and group reported that the magnetic susceptibility in $Mn(TCNE)_x \bullet y(CH_2Cl_2)$ material can be regulated by excitation with visible light and the photoinduced magnetism can be retained for many days in low temperatures (T_C = 75 K) [3]. These advantages would make the molecular magnets a promising replacement of the traditional magnets in many fields like data storage, nanodevices, sensors, and quantum computing. Although real-life use of these magnets has not yet started in the industry, it would be possible in near future, thanks to the efforts of an increasing number of researchers working on developing efficient organic and molecular magnets. Several researchers have studied ferromagnetism, ferrimagnetism, and anti-ferromagnetism of molecule-based magnets. Ferromagnetism is a property seen in materials like iron, nickel, and cobalt. Ferromagnetic materials have spins coupled in the same direction, while anti-ferromagnetic materials have spins aligned in the opposite direction (Net moment is zero). Ferrimagnetic materials, like anti-ferromagnetic materials, have spins aligned in the opposite direction, but there is a net magnetic moment because the spins do not totally cancel each other. The critical temperature of a magnetic material is the temperature beyond which the magnetic properties of the material begin to disrupt. The critical temperature or Curie temperature (T_C) of Fe is 1043 K. The Curie temperature of Fe_3O_4, a ferrimagnetic material, is 858 K. For an antiferromagnetic material like MnO (T_N =116 K), this critical temperature is called Néel temperature (T_N). Most organic materials show magnetic ordering below room temperature, making them ineffectual in practical applications. For example, for an organic magnet $[Fe(C_4Me_5)_2]^+ [TCNE]^-$ the ferromagnetic ordering was seen for T_C = 4.8 K. Variants of $[Fe^{III}(C_5Me_5)_2]^+ [TCNE]^-$ material showed weak ferromagnetism at room temperature and was studied by Epstein and Miller [9].

Researchers are becoming increasingly interested in developing organic and molecule-based magnets showing magnetism at room temperature. In 1989, Johannsen and co-workers carried out an experiment where 1,3,5-triaminobenzene was reacted with aniline in CH_3COOH to form Poly(1,3,5-triaminobenzene). They reported that the precipitate formed minutes after the reaction started but it took two days for a visible polymerization at room temperature. The resulted polymer was light-tan colored and insoluble in ordinary solvents. It was considered a potential ferromagnetic polymer showing ferromagnetism at room temperature [4]. In 2004, Zaidi and co-workers synthesized an organic magnet that showed magnetism at room temperature. They worked on making a novel polymer called PANiCNQ by reacting polyaniline with tetracyanoquinodimethane. This newly developed material showed Curie temperature beyond 350 K [5]. PANI-Co polymer was synthesized by Li, Tang, and Kan in 2013. It showed ferromagnetism at room temperature [6]. PANiCNQ and other organic or molecular magnets possessing magnetism at room temperature are discussed in detail in the following section.

II. ROOM-TEMPERATURE ORGANIC AND MOLECULAR MAGNETS

A. *PANiCNQ:*

Zaidi, Giblin, Terry, and Monkman synthesized PANiCNQ using polyaniline (PANi) with tetracyanoquinodimethane (TCNQ) acting as an acceptor molecule. An intrinsic charge transfer phenomenon ensures radical development in this reaction. Synthesizing PANiCNQ was observed to be a kinetic reaction and thus showed changes in magnetism of the material with time. Upon magnetization of an initial diamagnetic sample for three months with a permanent magnet (200 mT), the mass magnetization went up to 0.1 $JT^{-1}Kg^{-1}$. The PANiCNQ material showed ferro and ferrimagnetism for a Curie temperature above 350 K. The formation of PANiCNQ is a hopeful development in organic magnet research [5].

B. *$V(TCNE)_x$•y(CH_2Cl_2):*

The $V(TCNE)_x$•y(Solvent) class of molecule-based magnets shows high magnetic ordering temperatures [9]. The $V(TCNE)_x$•y(CH_2Cl_2), where (x~2, y~1/2), is known to be the first room-temperature molecule-based magnet and has an approximate T_C of 400 K. This material was formed by Manriquez, Yee, McLean, Epstein, & Miller by adding $V(C_6H_6)_2$ to an excess of TCNE in a CH_2Cl_2 solvent at ambient temperature. The resulted material was a precipitate of an amorphous black solid. For ferromagnetic coupling, this material showed a total spin S=5/2 and magnetization M= $28*10^3$ emuG/mol [7].

C. *1,3,5-Triazine-Linked Porous Organic Radical Framework:*

Phan et al synthesized molecule-based material in which radicals were ferromagnetically coupled. The material exhibited spontaneous magnetization at room temperature. The hexacyanotrimethylenecyclopropanide radical anion $[CNCP]^-$ is used in the formation of the intended polymer because of the stability of the cyano-radical. The adjacent trimethylenecyclopropanide (CP) radical anions were observed to be in ferromagnetic coupling. The researchers polymerized the [CN6CP]K in relatively low temperature (300 °C) in vacuum by treatment with HOTf to diminish the probability of formation of metal impurities. The sample's color went from purple to black during the course of the reaction. The material showed $3.8*10^3$ emu•g^{-1} magnetic moment at room temperature. The critical temperature of the organic magnet was found to be 465 K [1].

D. *$KV^{II}[Cr^{III}(CN)_6]•2H_2O$:*

Holmes and Girolami carried out a research experiment describing the application of the sol-gel method in the synthesis of crystalline molecular magnets with Prussian blue structure. They discovered that their $KV^{II}[Cr^{III}(CN)_6]•2H_2O$ magnet possessed ferrimagnetism at room temperature and exhibited the magnetic ordering at temperature 376 K. This magnet was formed by treating $V(OTf)_2$ with $K_3[Cr(CN)_6]$. They found that it takes minimum 24 hours for the gel resulted from the reaction to convert into crystalline material. It was reported that the magnetic ordering temperature reduces to 365 K after frequently heating the sample at 400 K [8].

III. CONCLUSION

This review presents successful attempts by various researchers at synthesizing room-temperature organic and molecular magnets. As discussed in the previous section, organic and molecule-based magnets can be synthesized by using a variety of elements and methods. These magnets were reported to exhibit magnetic ordering at high temperatures—Magnet synthesized by Phan et al. showed critical temperature 465 K (191.85 °C). In the coming future, closer attention should be given to produce organic and molecular magnets having higher coercivity, higher critical temperature, and better structural properties. This new class of magnets is an interesting topic for research and it has the potential to become a practical application in the forthcoming years.

REFERENCES

[1]. Phan, H., Herng, T. S., Wang, D., Li, X., Zeng, W., Ding, J., ... & Wu, J. (2019). Room-temperature magnets based on 1, 3, 5-triazine-linked porous organic radical frameworks. Chem, 5(5), 1223-1234.
[2]. Miller, J. S. (2014). Organic-and molecule-based magnets. Materials Today, 17(5), 224-235.
[3]. Pejaković, D. A., Kitamura, C., Miller, J. S., & Epstein, A. J. (2002). Photoinduced Magnetization in the Organic-Based Magnet Mn (TCNE) x· y (CH 2 Cl 2). Physical review letters, 88(5), 057202.
[4]. Johannsen, I., Torrance, J. B., & Nazzal, A. (1989). A new electron rich network polymer: poly (1, 3, 5-triaminobenzene). Macromolecules, 22(2), 566-570.
[5]. Zaidi, N. A., Giblin, S. R., Terry, I., & Monkman, A. P. (2004). Room temperature magnetic order in an organic magnet derived from polyaniline. Polymer, 45(16), 5683-5689.
[6]. Li, S. Q., Tang, L., & Kan, J. Q. (2010). Synthesis and characterisation of PANI–Co in presence of magnetic field. Materials Research Innovations, 14(3), 262-267.
[7]. Manriquez, J. M., Yee, G. T., McLean, R. S., Epstein, A. J., & Miller, J. S. (1991). A room-temperature molecular/organic-based magnet. Science, 252(5011), 1415-1417.
[8]. Holmes, S. M., & Girolami, G. S. (1999). Sol− Gel Synthesis of KVII [CrIII (CN) 6]⊙ 2H2O: A Crystalline Molecule-Based Magnet with a Magnetic Ordering Temperature above 100° C. Journal of the American Chemical Society, 121(23), 5593-5594.
[9]. Epstein, A. J., & Miller, J. S. (1996). Molecule-and polymer-based magnets, a new frontier. Synthetic metals, 80(2), 231-237.