HOKKAIDO UNIVERSITY

Title	Multifunctional systems based on supramolecular motions in [Ni(dmit)2]- magnetic crystals [an abstract of entire text]
Author(s)	李, 思敏
Description	この博士論文全文の閲覧方法については、以下のサイトをご参照ください。 https://www.lib.hokudai.ac.jp/dissertations/copy-guides/
Degree Grantor	北海道大学
Degree Name	博士(環境科学)
Dissertation Number	甲第14344号
Issue Date	2021-03-25
Doc URL	https://hdl.handle.net/2115/82042
Type	doctoral thesis
File Information	Li_Simin_summary.pdf

Hokkaido University Collection of Scholarly and Academic Papers : HUSCAP

学 位 論 文 の 要 約

博士（環境科学）　　氏 名　LI SIMIN

学 位 論 文 題 名

Multifunctional systems based on supramolecular motions in $[Ni(dmit)_2]^-$ magnetic crystals

（$[Ni(dmit)_2]^-$磁性結晶における超分子運動に基づく複合機能系）

Supramolecules exhibit functions not only derived from each molecule but also those through the interaction between molecules, which cannot be realized by single molecule. Therefore, supramolecular approach is an effective way to design multifunctional materials. We have been studying on supramolecular crystals based on cationic supramolecules and electrically active $[Ni(dmit)_2]^-$ ($dmit^{2-}$ = 2-thioxo-1,3-dithiole-4,5-dithiolate) anion. The $[Ni(dmit)_2]^-$ anion has a π-conjugated system with an open-shell electric structure and can be used as an excellent building block to construct molecular magnets. Various assembly structures of $[Ni(dmit)_2]^-$ can be obtained by introducing different supramolecular cations in which molecular motions are retained. The dynamic structure of cations has a great influence on the molecular arrangement of $[Ni(dmit)_2]^-$, making the magnetic properties tailorable.

Based on these background, supramolecular crystals of $[Ni(dmit)_2]^-$ exhibiting more than two functions were designed and synthesized. Relationship between structure and physical properties were studied, emphasizing on correlation between the functions in a crystal. The thesis includes seven chapters. Chapter 1 introduced general background of this study, experimental details were described in the chapter 2, and conclusions were drawn in chapter 7.

In chapter 3, $HDABCO^+$ (DABCO = 1,4-diazabicyclo[2.2.2]octane) is combined with $[Ni(dmit)_2]^-$ to afford a highly symmetric crystal of $(HDABCO^+)_9(DABCO)[Ni(dmit)_2]_9 \cdot 6CH_3CN$ (**1**) with the space group of *R*-3 in trigonal crystal system. In the structure, $[Ni(dmit)_2]^-$ anions are arranged in a hexapetal flower-like channel structure through edge-on-type interactions and the channels that exist between the honeycomb distribution of $[Ni(dmit)_2]^-$ anions are filled with one-dimensional hydrogen bonding chain containing DABCO and CH_3CN. Five kinds of asymmetric DABCO and CH_3CN containing assemblies that comprise the one-dimensional chain in the crystal, where **A**

through **E** units are (CH_3CN-($HDABCO^+$)$_3$), ($HDABCO^+$-CH_3CN), (CH_3CN-$HDABCO^+$), (($HDABCO^+$)$_2$-(CH_3CN)$_3$), and ($HDABCO^+$)$_2$(DABCO), respectively. Each chain is comprised of the array **A**-**B**-**C**-**D**-**E**-**E′**-**D′**-**C′**-**B′**-**A′** where units with "prime" are generated by inversion of the original molecular assemblies. A total of 28 DABCO, CH_3CN and (CH_3CN)$_3$ components along with 18 protons are present along more than 150 Å long *c*-axis of each unit cell. The $[Ni(dmit)_2]^-$ in the framework are composed of two kinds of hexamers, which form trimer units. Interestingly, rather strong antiferromagnetic interaction dominates in the hexamers, whereas the hexamers interact with one another ferromagnetically. In the low temperature range, the magnetic properties are dominated by antiferromagnetic interactions in the whole crystal of **1**. The flexible nature of the DABCO/CH_3CN hydrogen bonding array in the channel are confirmed by the dielectric relaxation. Because the crystal of **1** does not contain a uniform DABCO chain in the channels, its dielectric response is limited to those arising from weak relaxation of molecular motion. Considering that $HDABCO^+$ has a length along the channel of ca. 5.2 Å, an ideal crystal **1** should contain 29 DABCO units along with 18 protons in its unit cell. Such crystals might have been present among the large number of polymorphs and pseudo polymorphs of (DABCO)-$[Ni(dmit)_2]$ that can be generated. This work provides new insight into strategies for designing crystals with electric (dielectric as well as conducting) and magnetic functions. From a magnetic perspective, space groups of the crystals in trigonal crystal system such as R-3 are interesting as candidates for spin frustration systems. Moreover, protonated DABCO chains are possibly important components of crystals that undergo ferroelectric phase transition. Besides, helical arrays of $[Ni(dmit)_2]^-$ anion radicals should exhibit peculiar magnetic and/or conducting properties such as chiral magnetism. Finally, correlations between these properties will lead to multifunctional systems such as multiferroics.

Chapter 4 is the investigation of molecular rotation and reversible water adsorption associated with magnetic switching in a single crystal without rigid molecular framework. In the section, dibenzo[24]crown-8 is used to build a flexible framework. The supramolecular cation is constituted by dibenzo[24]crown-8, 4-$ApyH^+$ (4-aminopyridinium) and H_2O molecules. Two hydrated polymorphs, namely, (dibenzo[24]crown-8)(4-$ApyH^+$)$[Ni(dmit)_2]$•H_2O (**2**•H_2O) and (dibenzo[24]crown-8)(4-$ApyH^+$)$[Ni(dmit)_2]$•0.4H_2O (**3**•H_2O) were synthesized by using different solvents. In both crystals, supramolecular cations form one-dimensional channel structure through π-π interaction, which are aligned between two-dimensional layers of $[Ni(dmit)_2]^-$. However, 4-$ApyH^+$ and H_2O within supramolecular assemblies in **2**•H_2O are ordered, that in **3**•H_2O are disordered in two positions. Although the crystals have no rigid molecular

framework like porous coordination polymers, **2**•H_2O can lose 0.7 molecules of H_2O while maintaining their crystalline state when undergoing heat treatment, which affords **2**•0.3H_2O. In turn, the obtained **2**•0.3H_2O can again adsorb H_2O by exposing to air returning to the original hydrated state of **2**•H_2O. During the ad/desorption processes, the overall crystal structure is not changed significantly except for small contraction or expansion of the dibenzo[24]crown-8 column. Upon desorption of H_2O, the 4-ApyH^+ cations rotated to fill the space originally occupied by H_2O, resulting in the crystallographic disordered 4-ApyH^+ in **2**•0.3H_2O. In the adsorption process, the H_2O molecules are transported through the channel by the aid of 4-ApyH^+ rotation and at the same time, 4-ApyH^+ returns to the ordered state again. Dibenzo[24]crown-8 also contribute to this process through expansion. This is consistent well with the ad/desorption result. Due to the unique mechanism, significant isotope effect is observed between the adsorption kinetics of H_2O and D_2O. The stronger antiferromagnetic interaction in dehydrated compound corresponded to closer molecular contacts due to slight shrinkage of the crystal upon desorption of H_2O molecules. The H_2O molecules in **3**•H_2O can also be removed by heating. The obtained (4-ApyH^+)(dibenzo[24]crown-8)[Ni(dmit)$_2$] (**3**) belongs to a more symmetric space group. In the crystal, 4-ApyH^+ within supramolecular cations becomes disordered over four sites, while the entire crystal frame remains unchanged. Temperature-dependent magnetic susceptibility reveals that almost the same antiferromagnetic exchange interactions occurred between [Ni(dmit)$_2$]$^-$ molecules in both hydrated crystal of **3**•H_2O and dehydrated crystal of **3**.

In chapter 5, the supramolecular cations prepared from the self-assembly of monoprotonated x-ApyH^+ (x = 3 or 4) cations and crown ethers (benzo[18]-crown-6 or [18]-crown-6), are introduced into the anionic radical salt [Ni(dmit)$_2$]$^-$ as counteractions, thus generating six novel compounds of (3-ApyH^+)(benzo[18]crown-6)[Ni(dmit)$_2$] (**4**), (4-ApyH^+)(benzo[18]crown-6)[Ni(dmit)$_2$] (**5**) (with disordered 4-ApyH^+), (4-ApyH^+)(benzo[18]crown-6)[Ni(dmit)$_2$] (**6**) (with ordered 4-ApyH^+), (3-ApyH^+)([18]crown-6)[Ni(dmit)$_2$] (**7**) (with ordered [Ni(dmit)$_2$]$^-$), (3-ApyH^+)([18]crown-6)[Ni(dmit)$_2$] (**8**) (with disordered [Ni(dmit)$_2$]$^-$), and (4-ApyH^+)([18]crown-6)[Ni(dmit)$_2$] (**9**). The crystal structures, dielectric properties and magnetic susceptibilities of these compounds are examined. Although they all form an arrangement of one-dimensional supramolecular columns separated by [Ni(dmit)$_2$]$^-$ anions, different supramolecular cations play different regulatory effects on the crystal structures and physical properties. Crystal **4**, **8** and **9** crystallize in polar space groups, while crystal **5**, **6** and **7** in non-polar one. Among them, polymorphs **5** and **6** exhibit different dielectric responses induced by molecular motions of different origins. This effect also leads to different magnetic

properties. Both of **7** and **8** are constructed by the same supramolecular assembly (3-ApyH$^+$)([18]-crown-6), but they show different polarity characteristics. The crystals **8** and **9** have similar crystal structures where the $[Ni(dmit)_2]^-$ dimers are disordered in two positions due to the rotation of the supramolecular cations, even though they are synthesized from different supramolecular assemblies. All crystals are antiferromagnetic, but various arrangements of $[Ni(dmit)_2]^-$ exhibit diverse intermolecular interactions and thus the antiferromagnetic behavior of the crystals are also distinct. The dielectric responses associated with molecular motion at different temperatures can be observed in crystals of **5** ~ **9**, while **4** is a semiconductor. We believe that more detailed research will promote further understanding of crystal self-assembly behavior, and thus provide more beneficial information for crystal design and synthesis.

In chapter 6, to investigate the chiral intermolecular interaction between sulfur-rich planar π-conjugated $[Ni(dmit)_2]^-$ anions, chiral supramolecular cations assembled from (*R*)/(*S*)-DAP^{2+} (DAP = diaminopropane) and [18]crown-6 are successfully introduced into $[Ni(dmit)_2]^-$ salts. Two types of solvent-controlled chiral $[Ni(dmit)_2]^-$ salts are prepared. The conformations of supramolecular cations differed from each other by using different solvents, which also regulated the arrangement of $[Ni(dmit)_2]^-$ anions and further magnetic properties. The crystal obtained in CH_2Cl_2, ((*R*)-DAP^{2+})$_3$([18]crown-6)$_6$[Ni(dmit)$_2$]$_6$•2CH_2Cl_2 (**10**) and ((*S*)-DAP^{2+})$_3$([18]crown-6)$_6$[Ni(dmit)$_2$]$_6$•2CH_2Cl_2 (**11**), formed chiral spiral column in which every three supramolecular cations are separated by CH_2Cl_2 molecules and surrounded by $[Ni(dmit)_2]^-$ anions which also form chiral network. While in the crystals obtained in CH_3CN, ((*R*)-DAP^{2+})([18]crown-6)$_2$[Ni(dmit)$_2$]$_4$•CH_3CN (**12**) and ((*S*)-DAP^{2+})([18]crown-6)$_2$[Ni(dmit)$_2$]$_4$•CH_3CN (**13**), $[Ni(dmit)_2]^-$ anions are partially oxidized with the average charge of -0.5. Two independent arrangements of $[Ni(dmit)_2]$ are observed in the same crystal, each of them is composed of $[Ni(dmit)_2]^-$ and $[Ni(dmit)_2]_3^-$, respectively. The dynamic motions of (*R*)/(*S*)-DAP^{2+} cations and crown ethers corresponding to the dielectric responses are also illustrated.

In this thesis, supramolecular crystals based on electronically active $[Ni(dmit)_2]$ anions and supramolecular cationic systems with potential electric functions associated with molecular motions constructed through hydrogen bonds has been studied. In total 13 crystals have been designed and investigated. Present study provides new insights into developing synergetic functions by introducing dynamic supramolecular structures into electrically and magnetically active single crystals.