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Title	Multifunctional systems based on supramolecular motions in [Ni(dmit)2]- magnetic crystals [an abstract of dissertation and a summary of dissertation review]
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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/2115/82041
Rights(URL)	https://creativecommons.org/licenses/by/4.0/
Type	doctoral thesis
File Information	Li_Simin_abstract.pdf, 論文内容の要旨

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学 位 論 文 内 容 の 要 旨

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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 $[Ni(dmit)_2]^-$, enabling 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 summarized in chapter 7.

In chapter 3, $HDABCO^+$ (DABCO = 1,4-diazabicyclo[2.2.2]octane) was 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. The $[Ni(dmit)_2]$ anions in **1** were arranged in a hexapetal flower-like channel structure through edge-on-type interactions and one-dimensional hydrogen bonding chain containing DABCO and CH_3CN was surrounded in the channel with a quite long *c* axis of more than 150 Å. The $[Ni(dmit)_2]^-$ in the framework was composed of two kinds of hexamers, which form trimer units.

Antiferromagnetic interaction dominates in the hexamers, whereas the hexamers interact with one another ferromagnetically. The flexible nature of the DABCO/CH_3CN array was confirmed by the dielectric relaxation.

In chapter 4, a hydrated crystal of (4-$ApyH^+$)(dibenzo[24]crown-8)[$Ni(dmit)_2$]•H_2O (**2**•H_2O) ($ApyH^+$ = aminopyridinium) was synthesized. In the crystal, supramolecular cations formed channel structure through π-π interaction, which were aligned between two-dimensional layers of $[Ni(dmit)_2]^-$. Although the crystals had no rigid molecular framework like porous coordination polymers, **2**•H_2O can lose 0.7 molecules of H_2O while maintaining their crystalline state by heat treatment. The obtained **2**•0.3H_2O can again adsorb H_2O by exposing to air returning to **2**•H_2O. During the ad/desorption processes, the overall crystal structure was 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. In the adsorption process, the H_2O molecules were transported through the channel by the aid of 4-$ApyH^+$ rotation. Due to the unique mechanism, significant isotope effect was observed between the ad/desorption of H_2O and D_2O. The stronger antiferromagnetic interaction between $[Ni(dmit)_2]^-$ was observed in **2**•0.3H_2O in comparison to **2**•H_2O, which was resulted from closer molecular contacts.

In chapter 5, four kinds of crystals, (3-$ApyH^+$)(benzo[18]crown-6)[$Ni(dmit)_2$] (**3**), (4-$ApyH^+$)(benzo[18]crown-6)[$Ni(dmit)_2$] (**4**), (3-$ApyH^+$)([18]crown-6)[$Ni(dmit)_2$] (**5**) and (4-$ApyH^+$)([18]crown-6)[$Ni(dmit)_2$] (**6**), were synthesized. In all crystals, crown ethers and $ApyH^+$ cations formed one-dimensional supramolecular columns which were separated by $[Ni(dmit)_2]^-$. Crystal **3** was a semiconductor while **4** exhibited a relaxation behavior above 240 K in dielectric measurements. Crystals **5** and **6** had similar crystal structures, where the $[Ni(dmit)_2]^-$ dimers were disordered in two positions due to the rotation of the supramolecular cations.

In chapter 6, chiral supramolecular cation of (*R*)- and ((*S*)-DAP^{2+})([18]crown-6)$_2$ (DAP = diaminopropane) were introduced into $[Ni(dmit)_2]^-$ salts. Two types of chiral compounds with different structures were obtained depending on solvents for the crystallization. The crystal obtained in CH_2Cl_2 had a chiral arrangement of $[Ni(dmit)_2]^-$ anions. On the other hand, $[Ni(dmit)_2]$ were partially oxidized with the average charge of –0.5 in the crystal obtained in CH_3CN. Two independent arrangements of $[Ni(dmit)_2]$ were observed, each of them was composed of $[Ni(dmit)_2]^-$ and $[Ni(dmit)_2]_3^-$.

In summary, present study brings new insights of developing synergetic functions by introducing dynamic supramolecular structures into electrically and magnetically active single crystals.