

ニッケルジチオレンアニオンラジカル中の水素結合型ポリロタキサン構造：構造相転移と関連した強磁性的および半導体特性

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Hydrogen-Bonded Polyrotaxane Cation Structure in Nickel Dithiolate Anion Radical Salts, Ferromagnetic and Semiconducting Behavior Associated with Structural Phase Transition

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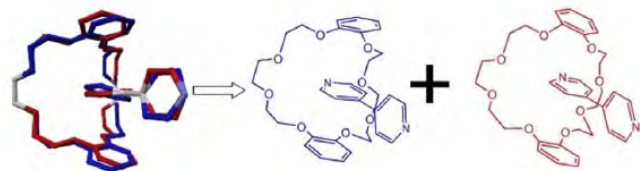


Figure 1. Disordered supramolecular cation structure in crystal 1.

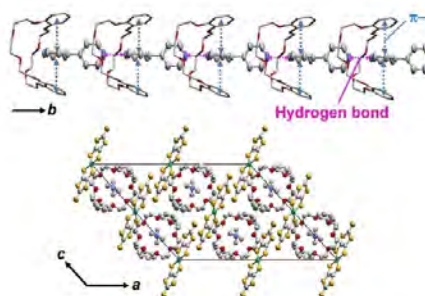


Figure 2. 1D pseudo-polyrotaxane structure formed by the 1D hydrogen-bonding polymer of (Hbpy⁺) **1** (upper). Packing structure of crystal **1** viewed along the b axis (lower).

2 研究所とのアライアンス共同研究

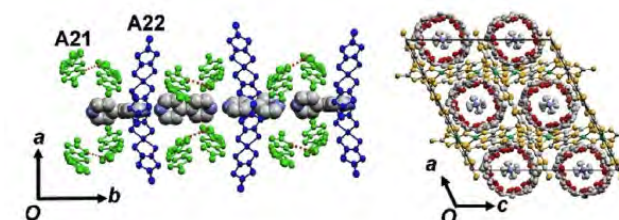


Figure 3. Arrangement of [Ni(dmit)₂] and H-bpy⁺ (left) and packing structure of crystal **2** viewed along the b axis (right).

The pseudo-polyrotaxane structure of [(H-bpy⁺)- (DB-24-crown-8)] has been incorporated into the anion radical salt [Ni(dmit)₂]. (H-bpy⁺)(DB-24-crown-8)[Ni(dmit)₂] crystallized as two polymorphs, crystals **1** and **2**. DB-24-crown-8 adopts a U-shaped conformation in which two phenylene rings sandwich one of the pyridyl rings of H-bpy⁺ to stabilize the structure. A structural phase transition was observed at 235 K, accompanied by ordering of the polyrotaxane structure.

擬ロタキサン構造[(H-bpy⁺)- (DB-24-crown-8)]を [Ni(dmit)₂]アニオンラジカル塩に導入したところ、結晶多型**1**と**2**が得られた。DB-24-crown-8は、U字型のコンフォメーションを取り、2つのフェニルユニットがピリジル環を挟み込むことで、擬ロタキサン構造の安定化が生じていた。また、ポリロタキサンの自由度を反映した構造相転移が235Kで観測された。