1. 有機ラジカル固体の物性科学
Solid-state properties of organic radicals

有機物の電気伝導体や磁気的性質などを調べる有機ラジカル固体の物性科学研究は、半世紀以上の歴史をもちます。その中で、もともとは低次元電子系として関心を集めた有機固体が、次元性の向上と分子間相互作用の高まりによって、きわめて多彩な性質を見せることが明らかになりました。我々は、相互作用の高次元化という視点から、有機と無機、分子とポリマーの境界上に位置するような環状チアジルラジカルや関連物質の研究を続けてきましたが、室温磁気双安定性、光誘起相転移、有機強磁性、２重融解、電子移動相転移、非線形電気伝導、電荷移動相転移、巨大過渡光電流など、さまざまな特性を見出しました。さらに最近では、立体的なπ電子系をもつ有機分子によって、3次元的な相互作用をもつ有機ラジカル固体の開発を進めています。

Research into the solid-state properties of organic radical solids has a long history of more than fifty years, focusing on molecular conductors and magnets. While most organic radical solids possess low-dimensional electronic states, improvements in the dimensionality and the interaction intensity have produced versatile physical properties. We have been working on the research into cyclic thiazyl radicals and their related compounds, which are quite unique chemical species, being on the borderlines between organic and inorganic, and between molecule and polymer, and, as such, we have observed unique physical properties, such as room-temperature magnetic bistability, photo-induced phase transitions, organic ferromagnetism, double melting, electron-transfer phase transitions, non-linear electrical transport, anomalous transient current, etc. Very recently, we have started working on 3D organic radical crystals, formed by polyhedron-shaped π-conjugated organic radicals.

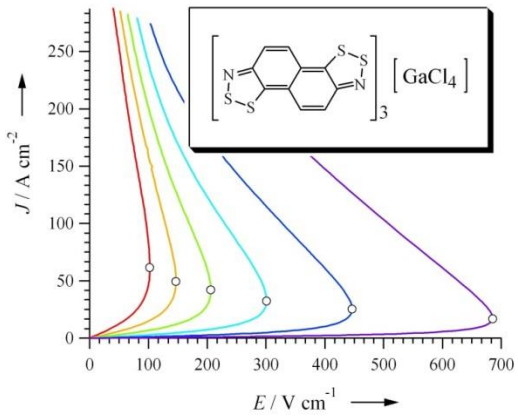

Fig. 1.　A thiazyl radical salt, $[NT]_3[GaCl_4]$, exhibites low-field negative resistance effects in a charge-ordered state on a square, columnar network of NT.

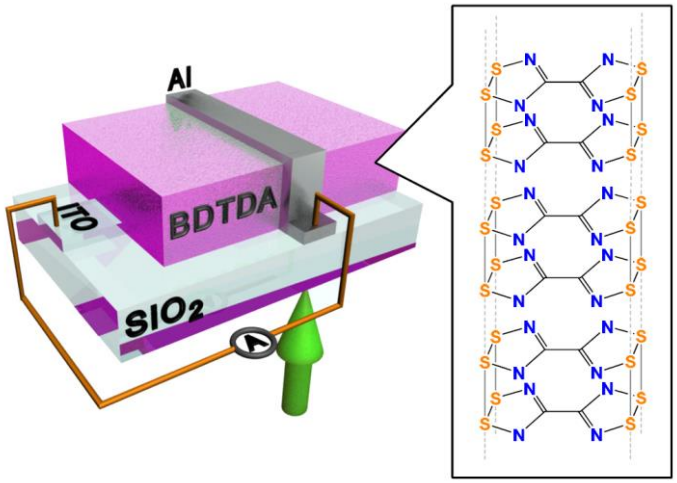

Fig. 2. A disjoint diradical, 4,4'-bis(1,2,3,5- dithiadiazolyl) (BDTDA), which makes highly oriented thin films with alternating π-stacking perpendicular to the substrates, exhibits a photocurrent with a high on/off ratio at reverse bias voltages, and photovoltaic behavior at zero bias voltage in ITO/BDTDA/Al sandwich-type cells**.**

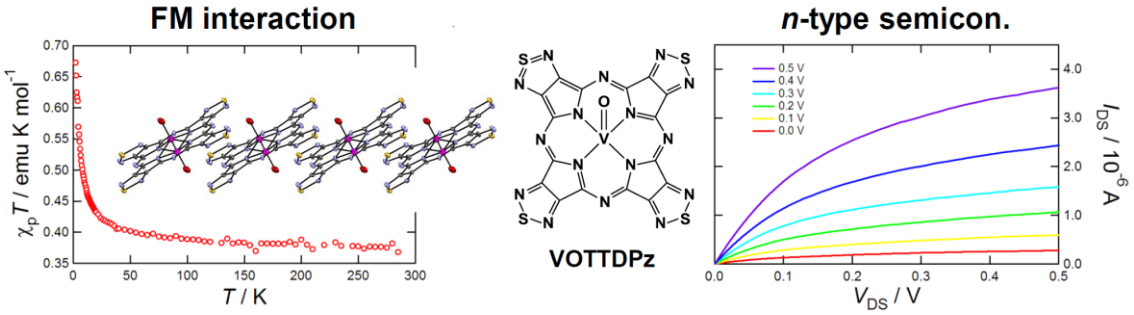

Fig. 3. Amorphous thin-film field-effect transistors of paramagnetic vanadyl tetrakis-(thiadiazole)-porphyrazine with ionic liquid gate dielectrics exhibit *n*-type performance with a high mobility of 2.8×10^{-2} $cm^2V^{-1}s^{-1}$ and an on/off ratio of 10^4.

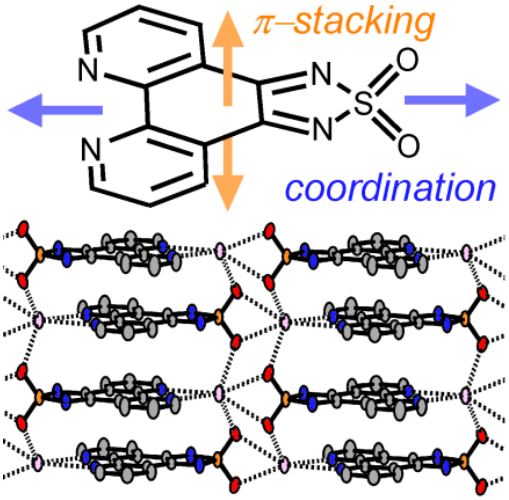

Fig. 4. A novel phenanthroline derivative, [1,2,5]thiadiazolo[3,4-*f*][1,10]phenanthroline ($tdapO_2$) was newly synthesized. Its radical anion, $tdapO_2$, acts as a bridging ligand, and forms multidimensional network structures. Magnetic property measurements reveal that such salts exhibit 1D antiferromagnetic interactions, and magnetic ordering below 15 K.

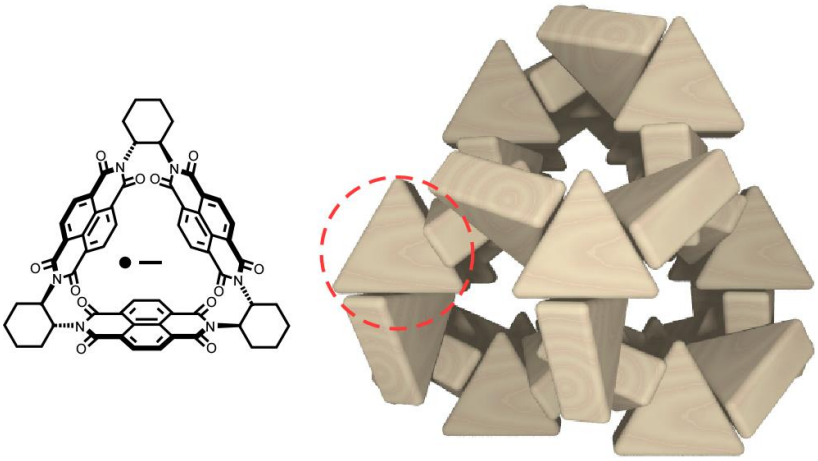

Fig. 5. We carried out electrochemical crystallization of the radical anion salts of NDI(naphthalene diimide)-Δ. X-ray crystal analysis revealed the K_4 structure, which was formed by the unique intermolecular π-overlap directed toward three directions from the triangular-shape NDI-Δ radical anions.

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