1. Solid-state properties of organic radicals

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[GaCl₄], exhibits 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 \( \pi \)-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 \( 2.8 \times 10^{-2} \text{ cm}^2\text{V}^{-1}\text{s}^{-1} \) 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)-\(\Delta\). X-ray crystal analysis revealed the \(K_4\) structure, which was formed by the unique intermolecular \(\pi\)-overlap directed toward three directions from the triangular-shape NDI-\(\Delta\) radical anions.
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