

Creation of Novel Photonic-Electronic-Magnetic Functions Based on Molecules with Open-Shell Electronic Structures

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Keywords

Radical, Open-Shell Electronic States, Photonic-Electronic-Magnetic Properties

The molecules with open-shell electronic states can exhibit unique properties, which are difficult to achieve for conventional closed-shell molecules. Our group develops new open-shell organic molecules (= radicals) and metal complexes to create novel photonic-electronic-magnetic functions.

While conventional closed-shell luminescent molecules have been extensively studied as promising components for organic light-emitting devices, the luminescent properties of radicals have been much less studied because of their rarity and low chemical (photo-)stability. We have developed highly photostable luminescent organic radicals, PyBTM and its analogues, and investigated photofunctions attributed to their open-shell electronic states. We have discovered that (i) PyBTM-doped molecular crystals exhibit photoluminescence at RT with $\phi_{em} = 89\%$, which is exceptionally high in radicals, (ii) radical-doped crystals and radical-based coordination polymers exhibit drastic changes in the emission spectra by applying a magnetic field. These are the first demonstrations of magnetoluminescence in radicals, and are attributed to interplay between the spin and the luminescence. Our studies provide novel and unique concepts in molecular photonics,

electronics, and spintronics, and also bring innovative ideas in the development of light-emitting devices.

Our group focuses on strongly-interacted spins in molecular crystals. The anisotropic assembly of open-shell molecules in crystalline states enables unique molecular materials with exotic electrical and magnetic properties, such as superconductors, ferromagnets, and quantum spin liquids.

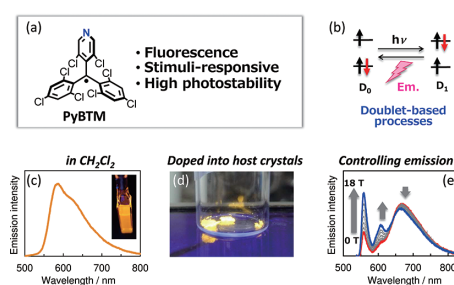


Figure 1. (a) Molecular structure of PyBTM and its characteristics. (b) Schematic photoexcitation-emission processes. (c) Emission in CH_2Cl_2 . (d) Emission of PyBTM-doped molecular crystals. (e) Controlling emission by magnetic field.

Selected Publications

- S. Kimura, M. Uejima, W. Ota, T. Sato, S. Kusaka, R. Matsuda, H. Nishihara and T. Kusamoto, "An Open-Shell, Luminescent, Two-Dimensional Coordination Polymer with a Honeycomb Lattice and Triangular Organic Radical," *J. Am. Chem. Soc.* **143**, 4329–4338 (2021).
- S. Kimura, T. Kusamoto, S. Kimura, K. Kato, Y. Teki and H. Nishihara, "Magnetoluminescence in a Photostable, Brightly Luminescent Organic Radical in a Rigid Environment," *Angew. Chem., Int. Ed.* **57**, 12711–12715 (2018).
- Y. Hattori, T. Kusamoto and H. Nishihara, "Enhanced Luminescent Properties of an Open-Shell (3,5-Dichloro-4-pyridyl)bis(2,4,6-trichlorophenyl)methyl Radical by Coordination to Gold," *Angew. Chem., Int. Ed.* **54**, 3731–3734 (2015).
- Y. Hattori, T. Kusamoto and H. Nishihara, "Luminescence, Stability, and Proton Response of an Open-Shell (3,5-Dichloro-4-pyridyl)bis(2,4,6-trichlorophenyl)methyl Radical," *Angew. Chem., Int. Ed.* **53**, 11845–11848 (2014).

1. A Novel Organic Quantum Spin Liquid Material with a Triangular Lattice

Quantum spin liquid (QSL) is a novel quantum state of matter, in which charges are localized while spins are highly fluctuating. In general, interacting spins with antiferromagnetic (AFM) exchange couplings result in long-range ordered magnetic ground state at low temperatures, with vanishing the spin entropy. On the other hand, spins in QSL that are entangled strongly remain highly fluctuating with high entropy even at very low temperatures. In QSL materials, geometrical frustrations, in addition to quantum fluctuations, are suggested to play a critical role. Among them, organic crystalline solids with triangular lattices have attracted much attention because of their intriguing properties at low temperatures. So far, organic QSL materials are rarely reported, which limits in-depth investigation for elucidating the fundamental characteristics of the QSL. In this study, we prepared a novel triangular-lattice organic QSL material (Et-4IT)[Ni(mnt)₂]₂, and the structure and physical properties were investigated (Figure 2a).¹⁾ The Ni(mnt)₂ anions constructed *k*-type molecular arrangement in the crystal. The two crystallographically independent anion layers both realized Mott insulating states, showing that (Et-4IT)[Ni(mnt)₂]₂ is a novel bilayer Mott system. The magnetic susceptibility and magnetic torque measurements and low-temperature heat capacity measurements confirmed the absence of the long-range magnetic ordering down to 25 mK with an appreciably significant γ value of 94 ± 7 mJ K⁻² mol⁻¹. The AFM interaction ($J/k_B \sim -24$ K) detected between the spins was much smaller than that in the other organic QSLs, while χ_0 and γ values were larger. We found significant relationships, $\chi_0, \gamma \propto 1/J$, for all the organic QSLs (Figure 2b). These results suggest the presence of the spinon Fermi surface in the QSLs.

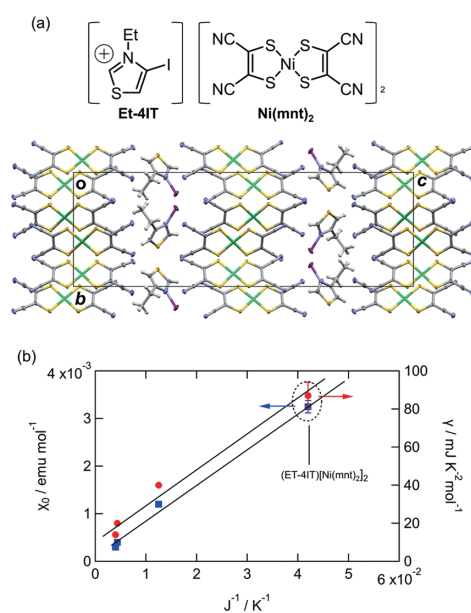


Figure 2. (a) Chemical and crystal structures of (Et-4IT)[Ni(mnt)₂]₂. (b) γ - J^{-1} and χ_0 - J^{-1} plots for organic QSLs.

2. Development of Two-Dimensional Kagome-Honeycomb Lattice Coordination Polymer Based on Triangular Radical

Two-dimensional (2D) open-shell coordination polymers (CPs) with honeycomb, Kagome, and Kagome-honeycomb hybrid lattices have attracted growing interest because of the exotic electronic structures and physical properties attributed to the structural topology. Employing organic radicals as building blocks is a promising approach to producing open-shell CPs, where structural topology and efficient electronic and magnetic interaction between the radical ligands and the metal ions enable peculiar electrical, magnetic, and photonic properties. Recently, we have prepared a highly-crystalline 2D honeycomb lattice CP, trisZn, via coordination of a triangular-shaped organic radical tris(3,5-dichloro-4-pyridyl)methyl radical (trisPyM) to Zn ions.²⁾ The coordination structure of trisZn was stable under evacuation at 60 °C. trisZn exhibited photoluminescence below 79 K at $\lambda_{em} = 695$ nm. Importantly, trisZn demonstrated magnetoluminescence below 20 K.³⁾ This is the first example showing magnetoluminescence of pure (*i.e.*, non-doped) radical compounds. trisPyM can be a promising building block in constructing a new class of 2D CPs with spin-correlated novel photofunctions. In this study, we aimed to create a Kagome-honeycomb hybrid lattice CP with magnetic functions by employing a magnetic ion Cu^{II} instead of the nonmagnetic Zn^{II}. The synthesized 2D CP, trisCu, was isostructural to trisZn, where the Cu^{II} ions constructed a Kagome lattice while trisPyMs formed a honeycomb lattice. In this situation, efficient magnetic couplings between the Cu^{II} ions and the radicals extended onto two dimensions were expected to induce strong magnetic anisotropy.

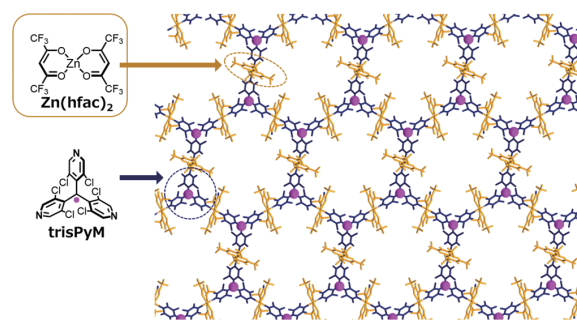


Figure 3. Crystal structure of trisZn and the chemical structure of the components.

References

- 1) T. Kusamoto, C. Ohde, S. Sugiura, S. Yamashita, R. Matsuoka, T. Terashima, Y. Nakazawa, H. Nishihara and S. Uji, *Bull. Chem. Soc. Jpn.* **95**, 306–313 (2022).
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