

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

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Professional Employment

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Awards

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2010 Research Award, Graduate School of Science, the University of Tokyo
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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.

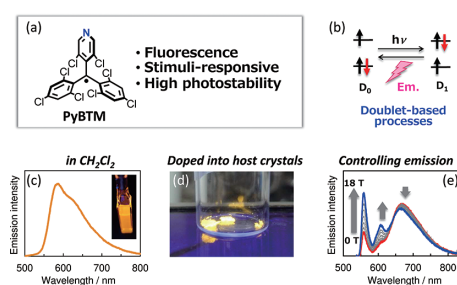


Figure 1. (a) Molecular structure of PyBTM and its characteristics. (b) Schematic photoexcitation-emission processes. (c) Emission in CH_2Cl_2 . (d) Emission of PyBTM-doped molecular crystals. (e) Controlling emission by magnetic field.

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. 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 (Figure 2).¹⁾ TrisZn demonstrated magnetoluminescence (MagLum) below 20 K.²⁾ This is the first example showing MagLum of pure (*i.e.*, non-doped) radical compounds.

Employing magnetic ions such as Cu^{II} ($S = 1/2$) and Ni^{II} ($S = 1$) instead of the nonmagnetic Zn^{II} is expected to enable Kagome-honeycomb hybrid lattices, where the magnetic ions and trisPyMs construct Kagome and honeycomb lattices, respectively. We prepared Cu^{II} and Ni^{II} Kagome-honeycomb hybrid lattices. Magnetic investigations indicated the emergence of long-range magnetic order and metamagnet-like behavior at low temperatures in these materials. Efficient magnetic couplings between the magnetic ions and the radicals extended onto two dimensions were expected to induce strong magnetic anisotropy.

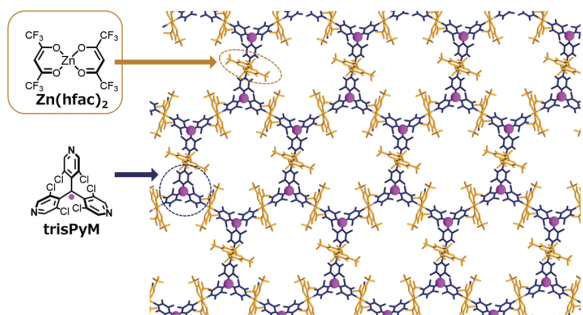


Figure 2. Crystal structure of trisZn and the chemical structure of the components.

2. Single-Molecule Magnetoluminescence from a Luminescent Diradical

Luminescent radicals attract increasing interest as a new class of materials that enable unique photofunctions not found in conventional closed-shell molecules due to their open-shell electronic structure. Particularly promising are photofunctions resulting from the correlation between the radical's spin and luminescence, such as MagLum, in which an external magnetic field reversibly controls the luminescence. Developing such photofunctions and elucidating their mechanisms would establish fundamental understandings that could be a basis for future spin-photonics and photo-spintronics. However, previous observations of MagLum in radicals have been limited to systems where radicals are randomly doped in host crystals or periodically arranged within the crystal lattices of the coordination polymer through metal complexation. This study shows that a diradical with covalently-linked two radical units within a single molecular skeleton can exhibit MagLum as a single-molecular property (Figure 3).³⁾ This enables the detailed elucidation of the requirements for and mechanisms of MagLum in assembled radicals and can aid the rational design of MagLum-active radicals based on synthetic chemistry.

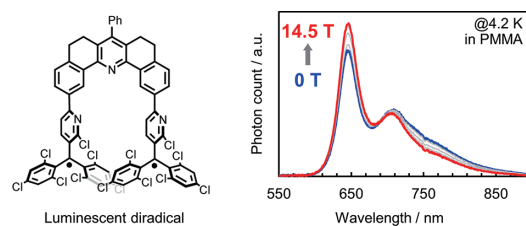


Figure 3. Chemical structure and magnetoluminescence at 4.2 K of a luminescent diradical.

References

- 1) S. Kimura, M. Uejima, W. Ota, T. Sato, S. Kusaka, R. Matsuda, H. Nishihara and T. Kusamoto, *J. Am. Chem. Soc.* **143**, 4329–4338 (2021).
- 2) S. Kimura, R. Matsuoka, S. Kimura, H. Nishihara and T. Kusamoto, *J. Am. Chem. Soc.* **143**, 5610–5615 (2021).
- 3) R. Matsuoka, S. Kimura, T. Miura, T. Ikoma and T. Kusamoto, *J. Am. Chem. Soc.* **145**, 13615–13622 (2023).