

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

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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 its 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.

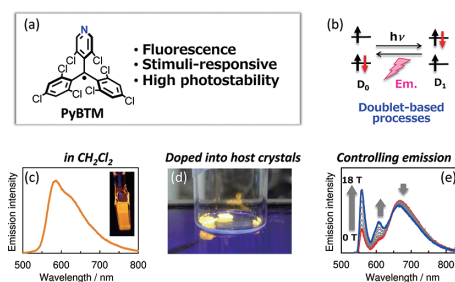


Figure 1. (a) Molecular structure of PyBTM and its characteristics. (b) Schematic photoexcitation-emission processes. (c) Emission in CH₂Cl₂. (d) Emission of PyBTM-doped molecular crystals. (e) Controlling emission by magnetic field.

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. An Open-Shell, Luminescent, Two-Dimensional Coordination Polymer with a Honeycomb Lattice Based on Triangular Radical

Two-dimensional (2D) open-shell coordination polymers (CPs) with honeycomb lattices have attracted growing interest because of the exotic electronic structures and physical properties derived from their structural topology. Employing organic radicals as building blocks is a promising approach to produce open-shell CPs. However, radical-based CPs with honeycomb lattices reported generally have low chemical stability or poor crystallinity. Accordingly, high crystallinity and persistence are in strong demand in this class of compounds. In this study, we developed a novel triangular organic radical tris(3,5-dichloro-4-pyridyl)methyl radical (trisPyM) possessing three pyridyl groups.¹⁾ trisPyM demonstrates photoluminescence ($\lambda_{\text{em}} = 700$ nm, $\phi_{\text{em}} = 0.85\%$, $\tau = 3.0$ ns in dichloromethane) and high photostability with its half-life upon UV irradiation 10000 times that of TTM, a conventional luminescent radical. Complexation of trisPyM with $\text{Zn}^{\text{II}}(\text{hfac})_2$ afforded single crystals of a novel 2D CP, trisZn, possessing a honeycomb lattice with graphene-like spin topology (Figure 2). The coordination structure of trisZn is stable under evacuation at 60 °C. trisZn exhibits photoluminescence below 79 K at $\lambda_{\text{em}} = 695$ nm. Importantly, trisZn displays magnetoluminescence below 20 K.²⁾ This is the first example showing magnetoluminescence as pure (*i.e.*, non-doped) radical compounds. Our results indicate that trisPyM can be a promising building block in the construction of a new class of 2D honeycomb CPs with spin-correlated novel photofunctions.

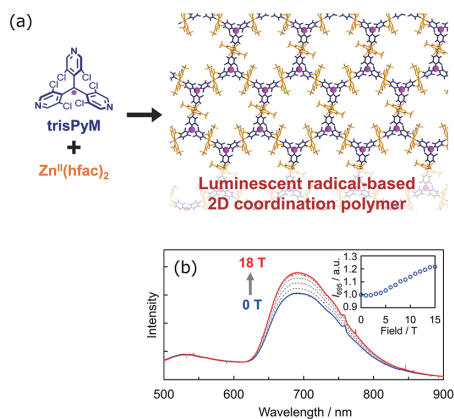


Figure 2. (a) Chemical structure of trisPyM and crystal structure of trisZn. (b) Emission spectra of trisZn at 4.2 K under a magnetic field.

2. Solid-State Room-Temperature Near-Infrared Photoluminescence of a Stable Organic Radical

Luminescent organic radicals have been shown to demonstrate unique emission properties in solvents or in host materials. On the other hand, the luminescent properties of radicals in the

fully aggregated pure solid state have rarely been investigated, especially at room temperature. In this study, a novel luminescent radical with a 3-pyridyl moiety, the (2,4-dichloro-3-pyridyl)bis(2,4,6-trichlorophenyl)methyl radical (metaPyBTM) was prepared and the optical properties were investigated in detail.³⁾ metaPyBTM exhibits distinct near-infrared photoluminescence in its crystalline state at room temperature, in spite of the fact that the electronic structure and photophysical properties in solution are similar to those of the analogues radicals. The solid-state luminescence properties of metaPyBTM are modulated strongly by temperature and the degree of aggregation. metaPyBTM in the moderately aggregated state displays magnetic-field responsive luminescence, magnetoluminescence, whereas no magnetic field effect was detected in the emission spectrum of purely crystalline metaPyBTM. These results suggest that controlling the manner of interactions between radicals is an important factor for achieving magnetoluminescence.

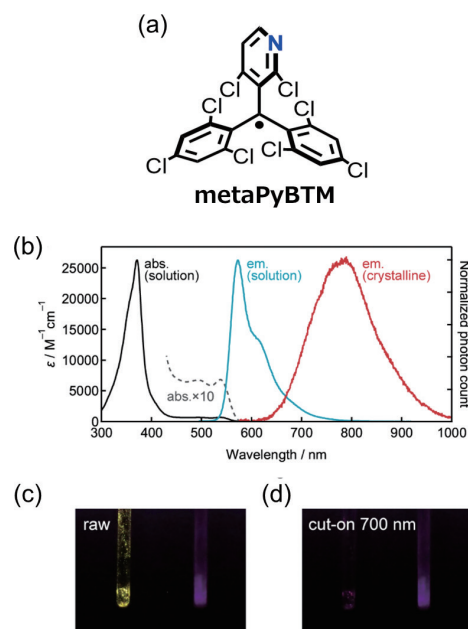


Figure 3. (a) Chemical structure of metaPyBTM. (b) Absorption and emission spectra of metaPyBTM in dichloromethane (black, pale-blue) and in crystalline state (red). (c,d) Vis-NIR photographs of pure metaPyBTM (right) and metaPyBTM-doped αH -metaPyBTM crystals under UV light at $\lambda = 365$ nm with (d) and without (c) a longpass filter (cut-on: 700 nm). Photos were taken by BIZWORKS Yubaflex digital camera.

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 and T. Kusamoto, *ChemPhotoChem* **5**, 669–673 (2021).