

# 論文の内容の要旨

## 論文題目

### Magnetoluminescence of Organic Radicals: Luminescence-Spin Correlated Properties Controlled by a Degree of Assembly

(有機ラジカルにおける磁場応答発光：  
凝集度により制御される発光 - スピン相関物性)

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## Introduction

Organic radicals have recently been attracting much attention as a new class of luminescent materials. Recent studies utilizing their unusual electronic structures based on the unpaired electrons have revealed their unique properties, such as 100% electron-photon conversion in light emitting devices and the absence of heavy atom effects. However, the luminescence properties of organic radicals have been studied far less than those of closed-shell molecules because they have long been thought as non-luminescent or highly light-sensitive species. Kusamoto *et al.* and my master course study have developed the photostable luminescent organic radicals, PyBTM and bisPyTM (Figure 1a). These radical species have one or two pyridyl rings in the framework of TTM (Figure 1a), which is unstable upon photoexcitation, allowing the emission characteristics of radicals to be investigated.

An important challenge remaining in the study of luminescent radicals is to develop photofunctions based on the interplay between luminescence and spin, which are difficult to achieve with conventional closed-shell molecules. In my doctoral course study, through developing new photostable luminescent radical materials, I aimed to establish magnetic field effects (MFEs) on luminescence (i.e., magnetoluminescence) as novel and unique photofunctions of organic radicals.

## A luminescent triarylmethyl radical with three pyridyl rings and its two-dimensional complexes

A novel stable organic radical with three pyridyl rings, tris(3,5-dichloro-4-pyridyl)methyl radical (trisPyM; Figure 1a) was synthesized and characterized by ESR spectroscopy, HR-ESI-MS, and single crystal XRD analysis. The emission spectrum of trisPyM in a  $\text{CH}_2\text{Cl}_2$  solution upon excitation at  $\lambda_{\text{ex}} = 350$  nm showed a broad band with an emission maximum wavelength of  $\lambda_{\text{em}} = 700$

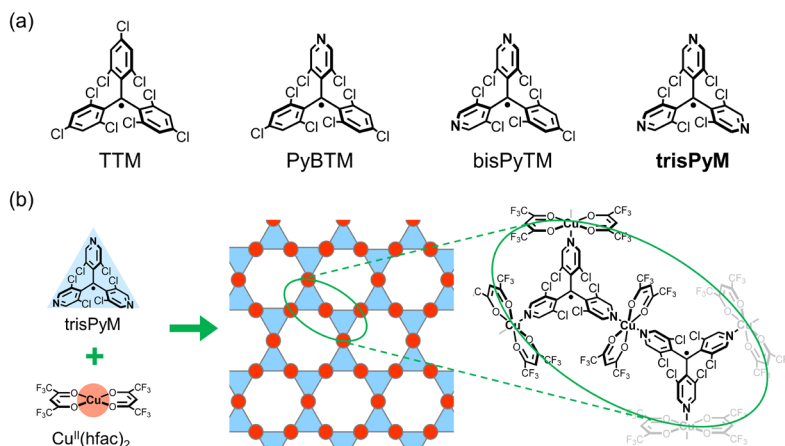


Figure 1. Chemical structures of (a) TTM, PyBTM, bisPyTM, and trisPyM and (b) **trisCu**.

nm and an absolute photoluminescence quantum yield of 1%. The luminescence of trisPyM was also observed in its solid state at 77 K with  $\lambda_{\text{em}} = 670$  nm. The photostability of trisPyM is 4 and 150 times higher than those of bisPyTM and PyBTM, respectively.

The three nitrogen atoms of trisPyM can act as the coordination sites; complexations between trisPyM and metal ions capable of axial coordination can afford two-dimensional coordination polymers with honeycomb structures. The molecular structure of  $[(\text{Cu}^{\text{II}}(\text{hfac})_2)_3(\text{trisPyM})_2]_n$  (**trisCu**; Figure 1b; hfac = hexafluoroacetylacetonato) was revealed by single crystal XRD analysis. The spin centers of trisPyM are located at the vertices of the slightly deformed honeycomb lattice while the  $\text{Cu}^{\text{II}}$  ions are placed at the midpoints of radicals, forming a kagome lattice. These results showed that

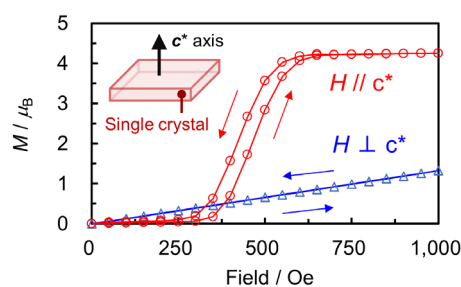


Figure 2.  $M$ - $H$  curves of **trisCu** at 2 K with  $H \parallel c^*$  and  $H \perp c^*$ . Inset shows the relationship between the shape of a crystal and the direction of the  $c^*$  axis.

trisPyM bore a luminescent property, high photostability, and coordination ability to construct defined two-dimensional polymers. Thus, it would be a promising building block to explore novel radical-based luminescence-magnetism correlated properties based on their low-dimensionality.

The magnetic susceptibilities of aligned platelet **trisCu** crystals were measured with magnetic fields perpendicular and parallel to the largest crystal planes ( $H \parallel c^*$  axis and  $H \perp c^*$  axis, respectively; Figure 2). Under  $H \parallel c^*$ , the magnetization vs. external magnetic field ( $M$ - $H$ ) curve of **trisCu** at 2 K displayed sudden increases in magnetization (spin-flip transition) at 250~350 Oe, and a hysteresis loop. In contrast, the magnetization increased gradually without hysteresis under  $H \perp c^*$  at 2 K. These behaviors were explained as the metamagnetic nature of **trisCu** based on the intralayer  $\text{Cu}^{\text{II}}$ -trisPyM ferromagnetic interactions and interlayer weak antiferromagnetic interactions, with its magnetic easy axis nearly parallel to the  $c^*$  axis.

## Magnetoluminescence of organic radical-based compounds

### Organic radicals doped in host matrices

In my master course study, I have found that the luminescence behaviors of  $\alpha H$ -PyBTM crystals doped with 10 wt% PyBTM (**Dope\_10**) at 4.2 K were modulated strongly by an external magnetic field (Figure 3a). This was the first example of the magnetic-field-sensitive luminescence properties of organic radicals; thus, understanding that the MFE mechanism would contribute hugely to exploring the magnetic-field-sensitive photofunctions of radicals.

Magnetic field (0-14 T) and temperature (4.2-20 K) dependences on the time-resolved emission of **Dope\_10** were examined by measuring emission decays of the monomer and excimer to elucidate the effect of the magnetic field on the excited-state characteristics (Figure 3b). A scheme for the MFE was constructed based on the results of the emission lifetime measurements. Quantum mechanical simulations for the decay curves based on the scheme disclosed the role of the magnetic field; it dominantly affects the spin sublevel population of radical dimers in the ground states. This situation is distinctly different from that in conventional closed-shell luminophores, where the magnetic field modulates their excited-state spin multiplicity (Figure 3cd). Namely, the spin degree of freedom of ground-state open-shell molecules is a new key for achieving magnetic-field-controlled molecular photofunctions.

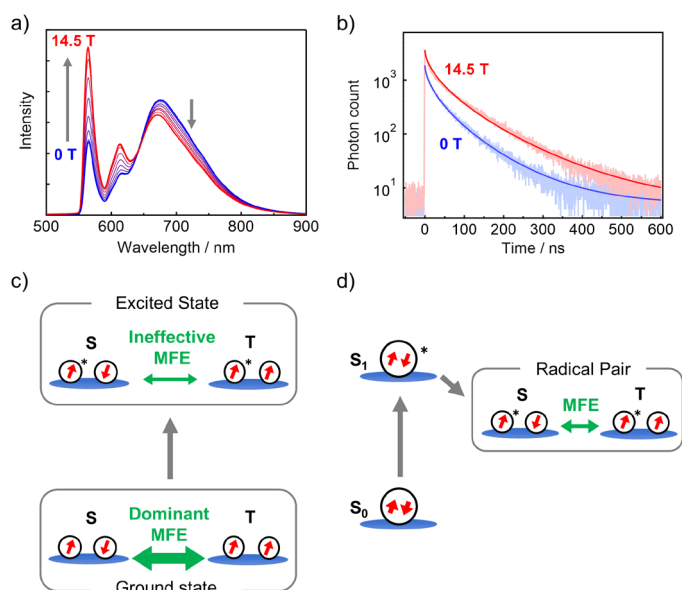


Figure 3. (a) Emission spectra and (b) emission decays at 563 nm of **Dope\_10** at 4.2 K under magnetic fields. Scheme of MFEs on (c) radicals (this system) and (d) conventional ground-state closed-shell molecules.

### Radical-ligated Zn<sup>II</sup> complexes doped in host matrices

The scope of candidate compounds showing magnetoluminescence should be expanded to provide new photofunctions in organic radicals. In this study, I prepared a radical-ligated metal complex, Zn<sup>II</sup>(hfac)<sub>2</sub>( $\alpha H$ -PyBTM)<sub>2</sub> (Fig. 4a) crystals in which  $\alpha H$ -PyBTM was substituted with PyBTM, and investigated their luminescent properties at different radical concentrations and under an applied magnetic field. The 5, 10, and 20

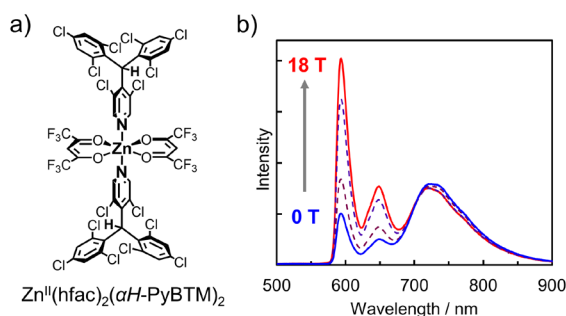


Figure 4. (a) Chemical structure of Zn<sup>II</sup>(hfac)<sub>2</sub> - ( $\alpha H$ -PyBTM)<sub>2</sub>. (b) Emission spectra of 20 wt%-substituted crystals at 4.2 K under a magnetic field.

wt%-substituted crystals displayed both monomer and excimer emissions, which were modulated strongly by the magnetic field (Figure 4b). Similarities in the magnetoluminescence behaviors between PyBTM and its  $\text{Zn}^{\text{II}}$  complex indicate that the observed MFE is not compound-specific but common to luminescent doublet molecules.

### Radical-based $\text{Zn}^{\text{II}}$ complexes with 1D and 2D structures

The studies so far indicated that weak interactions between radicals were a key for realizing magnetoluminescence of radicals. To see how the dimensions of the assembly affect magnetoluminescence behaviors, I prepared two  $\text{Zn}^{\text{II}}$  complexes with luminescent radical ligands,  $[\text{Zn}^{\text{II}}(\text{hfac})_2(\text{bisPyTM})]_n$  (**bisZn**) with a 1D chain structure and  $[(\text{Zn}^{\text{II}}(\text{hfac})_2)_3(\text{trisPyTM})_2]_n$  (**trisZn**) possessing a 2D honeycomb structure, and investigated their emission properties. Single crystal XRD analyses revealed the chemical structures of

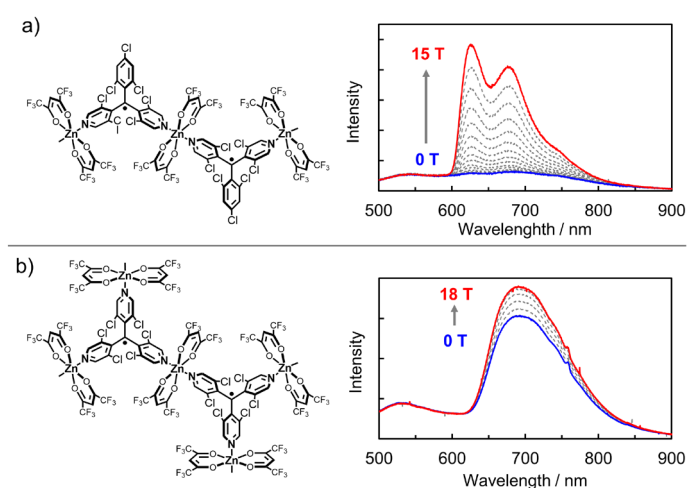


Figure 5. Chemical structure and emission spectra at 4.2 K under a magnetic field for (a) **bisZn** and (b) **trisZn**.

both complexes. While the ligand radicals, bisPyTM and trisPyM, showed negligible MFEs in their emission spectra, the luminescence of **bisZn** and **trisZn** displayed significant MFEs in the solid states at 4.2 K (Figure 5). **bisZn** was almost non-luminescent at 4.2 K under 0 T, and the emission band with the peaks at 625 and 676 nm appeared as the applied magnetic field increased. The emission of **trisZn** with the emission maximum of 693 nm was enhanced by applying magnetic field. These results indicated that 1D and 2D assemblies facilitated the weak radical-radical interactions, leading the magnetoluminescence.

### Conclusions

In the series of research, I have prepared novel luminescent radical and radical-ligated 0-2D complexes and investigated their magnetic and luminescent properties under applying magnetic field. As a result, the mechanism and methodologies for realizing magnetoluminescence of organic radicals have been proposed. The results demonstrated here first established a novel photofunctionality based on the interplay between luminescence and spins of radicals.