

## Spin-correlated Luminescence of Organic Radicals and Radical-based Metal Complexes

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### Introduction

Stable organic radicals have long been considered as non-emissive or highly light-sensitive species. Recent developments of luminescent radicals have revealed their unique emission characteristics based on the doublet states, such as efficient exciton generation in electroluminescent devices and the absence of heavy atom effect.<sup>1</sup> We have developed a highly photostable luminescent radical PyBTM (Figure 1a).<sup>2</sup> The photofunctions of PyBTM can be enhanced by coordination to metal ions; for example, the photoluminescence quantum yield, fluorescence wavelength, and the stability in the photoexcited state all increases upon coordination to Au<sup>1</sup>.<sup>3</sup>

One of the important challenges that remains unexplored in the studies of luminescent radicals is to develop photofunctions based on the interplay between luminescence and spin, which are difficult (or impossible) for conventional closed-shell photoemissive molecules to achieve. To tackle this challenge, I focus on magnetic-field-controlled photofunctions of radicals as their novel spin-correlated luminescence properties. Here I show recent progress on magnetic-field-responsive luminescence (i.e., magnetoluminescence) of radicals.

### Magnetoluminescence of radicals doped into solid matrix

We investigated the emission properties of PyBTM that was doped into host molecular crystals.<sup>4</sup> The 0.05 wt%-doped crystals displayed luminescence attributed to a radical monomer with a room-temperature emission quantum yield of 89%, which is exceptionally high among organic radicals. A new broad emission band assignable to an excimer emerged at longer wavelength region as the doping concentration increased. The 10 wt%-doped crystals displayed both PyBTM monomer-like and excimer-centered emission bands, and the intensity ratio of the two bands changed drastically by applying a magnetic field of up to 18 T at 4.2 K (Figure 1b). This is the first observation of magnetoluminescence of organic

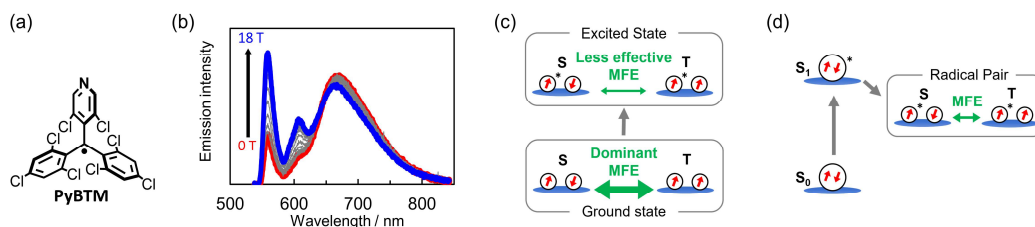


Figure 1. (a) Chemical structure of PyBTM. (b) Magnetic field dependence of emission spectra of 10 wt%-doped crystals at 4.2 K. (c,d) Scheme of magnetic field effects on (c) radicals in the present system and (d) conventional ground-state closed-shell molecules.

radicals. Detailed investigations on time-resolved emission and quantum mechanical simulations allowed to establish a plausible mechanism for the magnetoluminescence, then disclosed the role of the magnetic field; it dominantly affects the spin sublevel population of radical dimers in the ground states.<sup>5</sup> This situation is distinctly different from that in conventional closed-shell molecules, where the magnetic field modulate their excited-state spin multiplicity (Figures 1c,d). Namely, the spin degree of freedom of ground-state open-shell molecules is a new key for achieving magnetic-field-controlled molecular photofunctions. The magnetoluminescence could also be observed in the other radical or radical-Zn complex doping systems,<sup>6,7</sup> suggesting the generality of magnetic field effects on the luminescence of radicals.

#### Magnetoluminescence of radical-based 1D and 2D coordination polymers

Magnetoluminescence was shown to be achieved not only by radicals doped in host matrices but also by radicals periodically arranged in crystal lattices.<sup>8</sup> The luminescence properties of bisPyTM and trisPyM radicals and their 1D and 2D Zn<sup>II</sup> coordination polymers (CPs) were investigated (Figure 2). Although solid-state emissions of bisPyTM and trisPyM were not affected significantly by external magnetic field at 4.2 K, those of CPs were greatly modulated. We propose that the reduction of radical–radical interactions in CPs is a key for achieving magnetoluminescence. Because CPs have advantages in the molecular designability and property tunability, including inter-/intramolecular electronic and magnetic interactions, over randomly dispersed doping systems, the methodology developed here would contribute to molecular designs for developing spin-luminescence correlated phenomena.

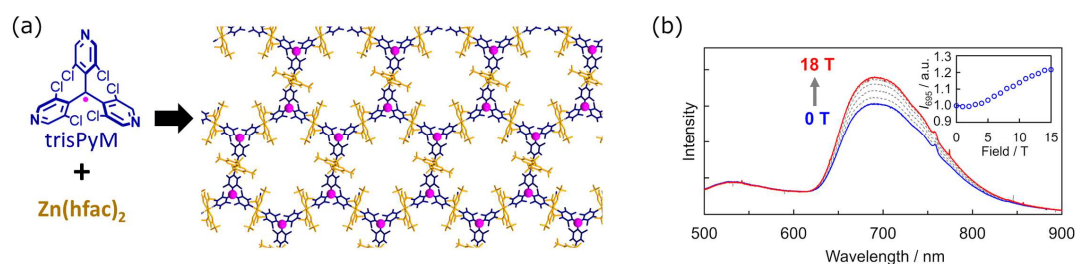


Figure 2. (a) Crystal structure of trisPyM-based 2D CP and chemical structures of its components (b) Magnetic field dependence of emission spectra of the 2D CP at 4.2 K.

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