

## Spin-correlated luminescence of radical-based molecular materials

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Stable organic radicals possess open-shell electronic states and exhibit vivid physical properties such as electrical conductivity and magnetism attributed to unpaired electrons. Their luminescence properties, however, have poorly been examined; they have long been considered as non-emissive or light-sensitive species. Recent developments of luminescent stable radicals have revealed their unique emission characteristics based on the doublet states, such as efficient generation of bright exciton in electroluminescent devices and the absence of heavy atom effect. Our group has developed photostable luminescent radicals with pyridyl groups within the triarylmethyl radical skeleton, such as PyBTM (Figure 1a).<sup>1,2</sup> The luminescence properties of PyBTM can be modulated by coordination to metal ions; for example, the photoluminescence quantum yield and emission wavelength increased upon coordination to Au.<sup>1,3</sup>

An important issue that remains to be explored in radicals is to develop photofunctions based on the interplay between spin and luminescence; such functions would be difficult (or impossible) to achieve with conventional closed-shell molecules. Our recent studies on luminescent radicals have revealed that aggregated radicals can exhibit magnetic-field-controlled luminescence (magnetoluminescence, MagLum), where the spin states correlate strongly with the emission dynamics. Here I would like to present radical-based materials showing MagLum.

**MagLum of radicals doped into host molecular crystals:** We investigated the emission properties of PyBTM 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 a longer wavelength region in the emission spectra with increasing doping concentration. The 10 wt%-doped crystals displayed both PyBTM monomer-like and excimer-like emission bands. The intensity ratio

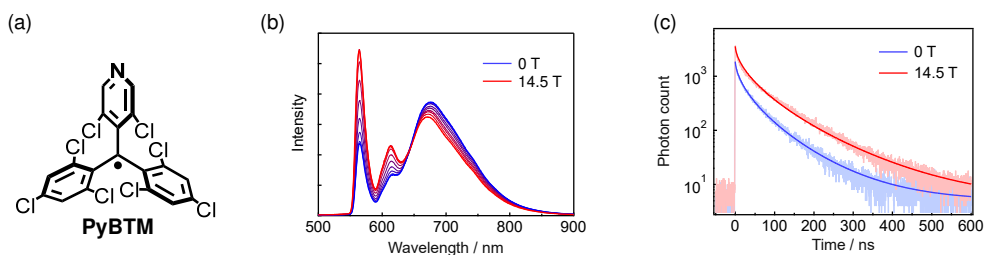


Figure 1. (a) Chemical structure of PyBTM. (b,c) Magnetic field dependence of emission spectra (b) and emission decay profiles (c) of 10 wt%-doped crystals at 4.2 K. Blue and red curves in (c) are simulated ones.

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 MagLum in organic radicals. Detailed investigations on time-resolved emission and quantum mechanical simulations (Figure 1c) allowed us to establish a plausible mechanism for the MagLum, where the magnetic field dominantly affects the spin sublevel population of radical dimers in the ground states.<sup>5</sup> MagLum 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. These studies show that the spin degree of freedom in the ground state can be a key to achieving spin-correlated photofunctions.

**MagLum of radical-based 1D and 2D coordination polymers:** Combination of bisPyTM or trisPyM and  $\text{Zn}(\text{hfac})_2$  resulted in open-shell 1D or 2D coordination polymers (CPs) demonstrating MagLum (Figure 2a).<sup>8</sup> While solid-state emissions of bisPyTM and trisPyM were not affected significantly by the external magnetic field at 4.2 K, those of the CPs were greatly modulated (Figure 2b). Reducing magnetic interactions between the radicals by forming CP structures was suggested to enable MagLum. Because CPs have advantages in molecular designability and property tunability, including inter-/intramolecular electronic and magnetic interactions, over randomly dispersed doping systems, the methodology developed here would contribute to developing spin-luminescence correlated phenomena.

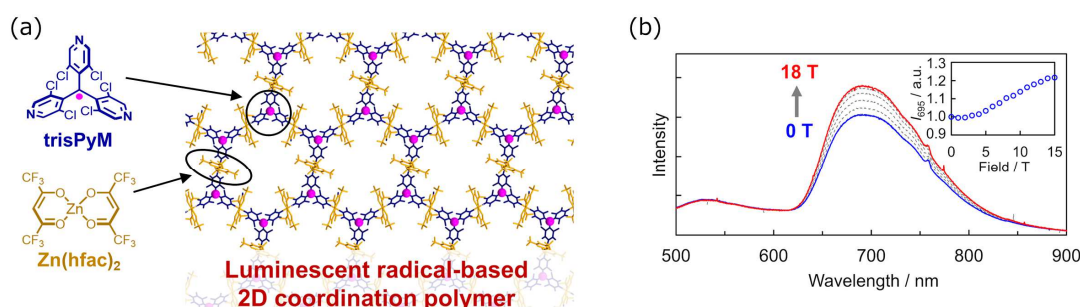


Figure 2. (a) Crystal structure of a trisPyM-based 2D CP and chemical structures of component molecules. (b) Magnetic field dependence of emission spectra of the 2D CP at 4.2 K.

## References

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