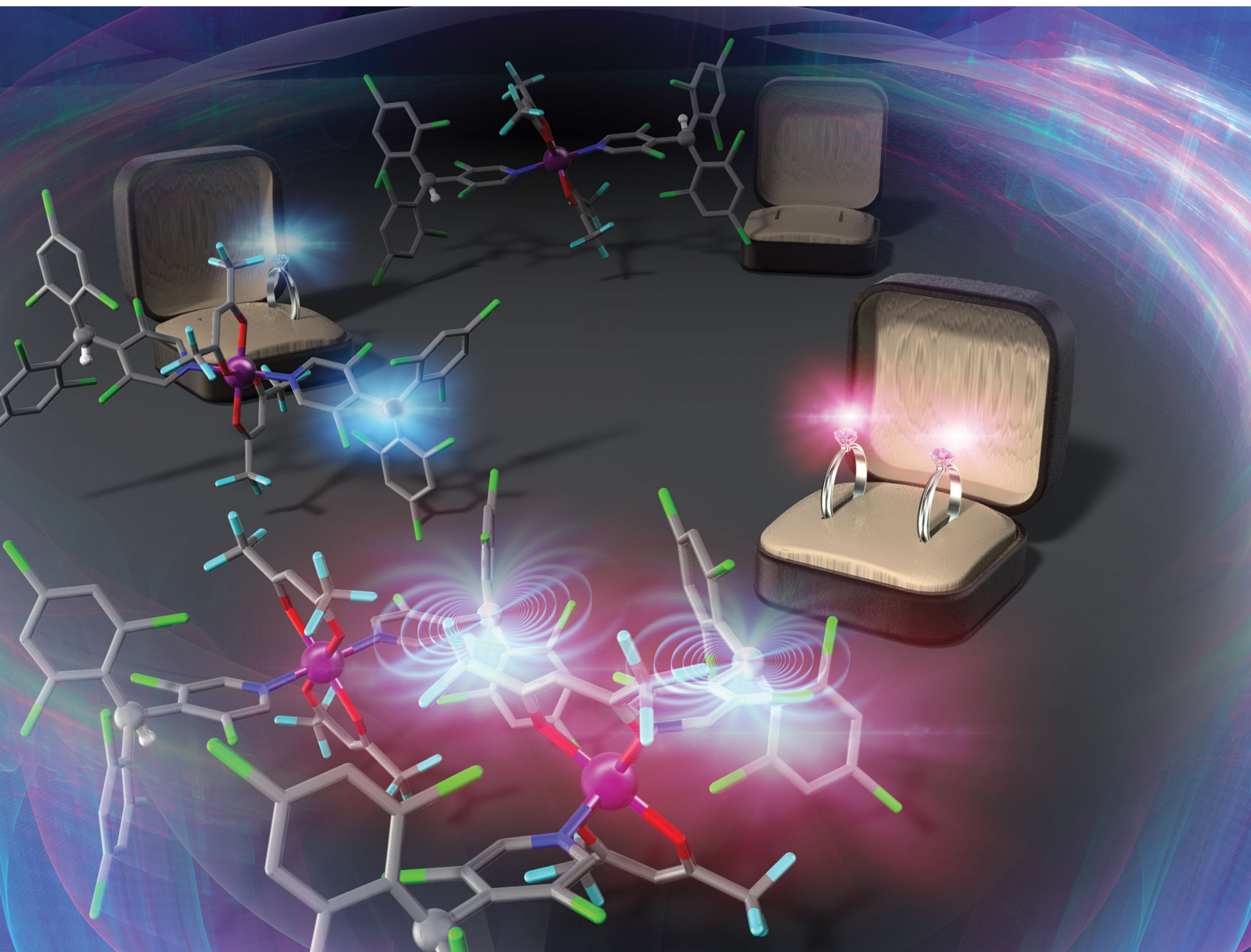


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Excimer emission and magnetoluminescence of radical-based zinc(II) complexes doped in host crystals†

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A Zn^{II} complex based on a luminescent organic radical was doped into host molecular crystals. The 5, 10, and 20 wt%-doped crystals showed excimer emissions and their luminescent behaviours were significantly modulated by an external magnetic field. These are the first examples showing excimer emissions and magnetic-field-sensitive luminescent properties for complexes based on luminescent radicals. The excimer species contributing to magnetoluminescence was determined by analyzing the emission spectra and their magnetic-field dependencies. These results suggest the general nature of magnetic field effects on the luminescence of radicals as well as the importance of the type of interaction between radicals.

Luminescent organic molecules have been developed for wide-ranging applications, including organic light-emitting diodes (OLEDs)¹ and bioimaging.² Recently, luminescent radicals have attracted much attention^{3–6} because of their unusual characteristics, such as long-wavelength emissions, the absence of heavy-atom effect, and the high electron–photon conversion efficiency of OLEDs. These properties arise from the unique spin states of radical molecules with an unpaired electron, so that controlling the spin state is the key to new photochemical and photophysical properties, which are difficult

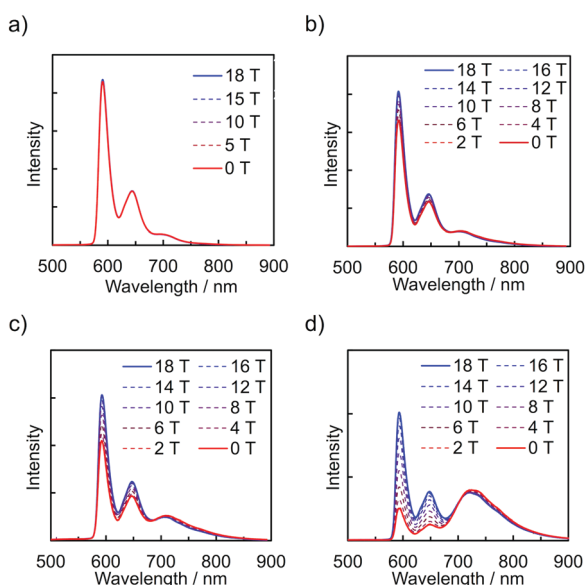
are the first reports of luminescent radical-coordinated metal complexes displaying excimer emissions. Their luminescent behaviours were modulated substantially by an external magnetic field, suggesting that magnetic-field-sensitive emission properties may be common, even in metal complexes with luminescent radicals. Two types of spin multiplicity changes, which would contribute to the MFE, were assumed to occur in this system: intramolecular changes in $\text{Zn}^{\text{II}}(\text{hfac})_2(\text{PyBTM})_2$ (Fig. 1b) and intermolecular changes in the $\text{Zn}^{\text{II}}(\text{hfac})_2(\alpha\text{H-PyBTM})(\text{PyBTM})$ dimer (Fig. 1c). Here we discuss which of these changes contributed to the magnetoluminescence.

$\text{Zn}^{\text{II}}(\text{hfac})_2(\alpha\text{H-PyBTM})_2$ was synthesized and characterized by the procedure described in the ESI†. A single-crystal X-ray diffraction study revealed the crystal structure of $\text{Zn}^{\text{II}}(\text{hfac})_2(\alpha\text{H-PyBTM})_2$ with the triclinic space group $P\bar{1}$ (Fig. 2). The unit cell contains two crystallographically independent $\text{Zn}^{\text{II}}(\text{hfac})_2(\alpha\text{H-PyBTM})_2$ molecules with almost identical structures. The $\text{Zn}^{\text{II}}(\text{hfac})_2(\alpha\text{H-PyBTM})_2$ crystals were isostructural with $\text{Zn}^{\text{II}}(\text{hfac})_2(\text{PyBTM})_2$ crystals⁹ except for the positions of the central carbon atoms of two (αH -PyBTMs), which were sp^3 -hybridized and disordered into two positions in the former crystals while sp^2 -hybridized in the latter. In one of the two crystallographically independent molecules, the trifluoromethyl groups in the hfac ligands were also disordered in two positions.

PyBTM-substituted $\text{Zn}^{\text{II}}(\text{hfac})_2(\alpha\text{H-PyBTM})_2$ with various PyBTM concentrations (1, 5, 10, and 20 wt% with respect to the sum of $\alpha\text{H-PyBTM}$ and PyBTM in the crystals) were prepared as follows. PyBTM, $\alpha\text{H-PyBTM}$, and $\text{Zn}^{\text{II}}(\text{hfac})_2$ were dissolved in dry dichloromethane. The solvent was allowed to evaporate slowly under dark and ambient conditions and the

yield, ϕ_{em} , of 18%; as the radical concentration increased, the excimer emission appeared and the ϕ_{em} value of **PyZn_R** decreased to 5.2% for **PyZn_20**. This is explained by concentration quenching in the crystals, with the quantum yield of excimer emission being lower than that of monomer emission. The emission lifetime at the excimer-centred emission wavelengths for **PyZn_5**, **PyZn_10**, and **PyZn_20** was longer than that at the monomer-centred emission wavelengths and the emission decay could be fitted with a single exponential curve (Fig. S6, ESI†). This indicates that the excimer was a single component, and thus either $\text{Zn}^{\text{II}}(\text{hfac})_2(\alpha\text{H-PyBTM})_2$ or the $\text{Zn}^{\text{II}}(\text{hfac})_2(\alpha\text{H-PyBTM})(\text{PyBTM})$ dimer was emissive.

The emission spectra of **PyZn_R** under an external magnetic field at 4.2 K were measured to investigate the MFE on the luminescent behaviour. Fig. 4a shows the emission spectra of **PyZn_1**, which displayed only monomer-centred emission, under applied magnetic fields of 0, 5, 10, 15, and 18 T. The spectra were not affected by these magnetic fields, suggesting an absence of MFE. This is consistent with our previous report, in which isolated PyBTM did not show an MFE because of its luminescent character being based on a doublet-doublet transition.⁷ In contrast, the emissions of samples with higher radical concentrations, **PyZn_5**, **PyZn_10**, and **PyZn_20**, which displayed monomer- and excimer-centred emissions, were clearly modulated by an external magnetic field (Fig. 4b–d). As the applied magnetic field increased, the monomer-centred emission at $\lambda_{\text{em}} = 595$ nm was strongly enhanced and the excimer-centred emission at $\lambda_{\text{em}} = 740$ nm was slightly suppressed. This is the first-reported example of an MFE observed for luminescent metal complexes with a coordinated luminescent radical. Fig. 5a and Fig. S7 (ESI†) show the intensity changes at monomer and excimer emission wavelengths for **PyZn_5**, **PyZn_10**, and **PyZn_20**. Different emission spectra of **PyZn_10** are shown in Fig. 5b. The magnitudes of the intensity



emission behaviours of **PyZn_R** under a magnetic field and that of **PyBTM**-doped α H-**PyBTM**, a similar mechanism for the MFE was expected, where the magnetic field modulates the spin multiplicity changes of the dimer in both the ground and excited states (Fig. S8, ESI†).^{7,8}

In conclusion, the luminescent behaviours of **PyBTM**-substituted $\text{Zn}^{\text{II}}(\text{hfac})_2(\alpha\text{H-PyBTM})_2$ crystals, **PyZn_R**, depend on the radical concentration and external magnetic field. **PyZn_1** displayed emission from the monomer $\text{Zn}^{\text{II}}(\text{hfac})_2(\alpha\text{H-PyBTM})(\text{PyBTM})$ and this emission was not magnetic-field-sensitive. In contrast, **PyZn_5**, **PyZn_10**, and **PyZn_20** displayed both monomer and excimer emissions, which were modulated strongly by the magnetic field. These are the first-reported examples of excimer emission and magnetoluminescence in luminescent radical-coordinated metal complexes. Considering their emission properties and MFE behaviours, the excimer emissive species was identified not as $\text{Zn}^{\text{II}}(\text{hfac})_2(\text{PyBTM})_2$ but as the $\text{Zn}^{\text{II}}(\text{hfac})_2(\alpha\text{H-PyBTM})(\text{PyBTM})$ dimer. These results suggest the general nature of MFEs on the luminescence of radicals¹⁵ as well as the importance of the type of interaction between radicals. Because complexation could modulate the inter/intramolecular interaction of spins, the development of MFEs on luminescent radical-ligated complexes would be a promising strategy, and this research surely is an important step in developing new photofunctions based on the interplay between spin and luminescence.

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