Supporting Information

Excimer emission and magnetoluminescence of radical-based

zinc(II) complexes doped in host crystals

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Materials and equipments

All chemicals were reagent grade and purchased commercially. Water was purified using AUTOPURE WD500 (Yamato Scientific Co., Ltd.). Dichloromethane (CH_2CI_2), diethyl ether (Et_2O), hexane and tetrahydrofuran (THF) used for syntheses were purified through organic solvent purifier (Nikko Hansen Co., Ltd.). PyBTM and α H-PyBTM were prepared by following procedures reported in the literature.¹

¹H and ¹³C NMR spectra were recorded with a JEOL JNM-ECS400 spectrometer at room temperature. Chemical shifts in ppm were referenced to tetramethylsilane (0.00 ppm) as an internal standard. Steady-state emission and excitation spectra at room temperature were measured with JASCO FP8600 spectrometers. Excitation spectra of PyZn_10 were measured by dispersing in water and corrected by subtracting those of Zn^{II}(hfac)₂(α H-PyBTM)₂. Sample solutions were bubbled with argon before measurement. Absolute photoluminescence quantum yields were measured with a Hamamatsu Photonics Quantaurus-QY C11347-01. Fluorescence lifetime measurements were performed using a measurement system with a picosecond diode laser with the emission wavelength of 375 nm (Advanced Laser Diode Systems PIL037X) as light source, a single grating spectrometer (Andor Kymera193i-B1), and a multichannel CCD detector (Andor iDus DV420A-OE). Powder X-ray diffraction were performed using Rigaku MiniFlex with Cu-*K* α radiation, operating at 40 kV and 15 mA.

The data for single crystal X-ray diffraction analysis were collected at 123 K on a ROD, Synergy Custom system (Rigaku Oxford Diffraction) equipped with mirror monochromated Mo- $K\alpha$ radiation. A suitable single crystal was mounted on a looped film (micromount) with Paraton-N. Data were processed using CrysAlisPro 1.171.39.43c (Rigaku Oxford Diffraction). The structure was solved using ShelXT² and the whole structure was refined against *F*² with SHELXL-2018/3.³ All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were located in idealized positions and were refined using a riding model with fixed thermal parameters. Crystal structure data (CIF, CCDC 2008148) can be obtained free of charge from The Cambridge Crystallographic Data Centre.

Synthesis of Zn^{II}(hfac)₂(αH-PyBTM)₂

Under nitrogen atmosphere, Zn^{II}(hfac)₂· 2H₂O (21.0 mg, 0.041 mmol) was dissolved in dry hexane (10 mL) under reflux. α H-PyBTM (46.0 mg, 0.088 mmol) dissolved in dry hexane (3 mL) and dry dichloromethane (1 mL) was added to the solution at 80°C, and stirred for 3hr. The resulted suspension was kept overnight at room temperature. The white precipitate was filtered, washed with hexane, and dried in vacuo. Recrystallization from dichloromethane-hexane afforded Zn^{II}(hfac)₂(α H-PyBTM)₂ (44.5 mg, 0.029 mmol) in 71% yield. Anal. Calcd for C46H16Cl16F12N2O4Zn: C, 36.32; H, 1.06; N, 1.84. Found: C, 36.01; H, 1.26; N, 1.95. ¹H NMR (400 MHz, CDCI₃) δ 8.48 (s, 1H), 8.35 (s, 1H), 7.41 (d, *J* = 2.2 Hz, 1H), 7.39 (d, *J* = 2.2 Hz, 1H), 7.29 (d, *J* = 2.1 Hz, 1H), 7.25 (d, *J* = 2.1 Hz, 1H), 6.72 (s, 1H), 6.12 (s, 1H). The peaks attributed to α H-PyBTM were almost matched with those of isolated α H-PyBTM in CDCI₃, ¹ suggesting the dissociation in CDCI₃. ¹³C NMR (100 MHz, CDCI₃) δ 180.5, 180.2, 179.8, 179.5, 148.6, 147.1, 146.9, 137.9, 137.5, 137.2, 137.1, 135.8, 134.8, 134.7, 132.2, 131.8, 130.4, 130.0, 128.8, 128.5, 121.5, 118.6, 115.8, 112.9, 90.0, 49.8.

Luminescence measurement under magnetic field

The system for luminescence measurement under magnetic field consists of a picosecond diode laser with the emission wavelength of 375 nm (Advanced Laser Diode Systems PIL037X) as light source, a single grating spectrometer (Andor Kymera193i-B1), and a multichannel CCD detector (Andor iDus DV420A-OE). This optical measurement system is combined with a solenoid type superconducting magnet, which can generate up to 18 T.⁴ Optical fibers are used to lead a light from light sources to a sample at the center of the superconducting magnet and from the sample to the spectrometer. The system of the vicinity of a sample follows the previous report.⁵

Deconvolution of the emission spectra of PyZn_5 and PyZn_10

The emission spectra of **PyZn_5** and **PyZn_10** were deconvoluted into monomer and excimer emission components. The emission spectrum of **PyZn_1** was utilized as the monomer emission component, which could be fitted to the sum of 4 Gaussian bands with wavenumber as the x-axis (Fig. S1a). Fig. S1b showed the excimer emission component, consisted of 2 Gaussian bands. The results of the deconvolutions were shown in Fig. S2 and Fig. 3ab shown in main text are the spectra where x-axes of Fig. S2 were converted into wavelength.



Fig. S1 (a) the monomer and (b) excimer emission components and their Gaussian bands used for the deconvolution of the emission spectra of **PyZn_5** and **PyZn_10**.



Fig. S2 Deconvolutions of emission spectra of (a) PyZn_5 and (b) PyZn_10.

radical concentration / wt%	<i>ø</i> em / %	τ 1 ⁵⁹⁵ /ns	τ2 ⁵⁹⁵ /ns	${ au_3}^{595}$ /ns	τ ₁ ⁷²⁵ /ns	τ ₂ ⁷²⁵ /ns
1	18	19	48	174	-	_
		(56)	(43)	(1.0)□		
5	11	7.9	25	153	20	862
		(63)	(35)	(2.0)	(87)	(13)
10	7	4.7	17	215-	21	771
		(73)	(26)	(1.7)□	(76)	(24)
20	6	1.8	11	245	32	746
		(90)	(8.0)	(1.7)	(18)	(82)

Table S1 Photophysical properties of PyZn_R

 τ_1^{595} , τ_2^{595} , τ_3^{595} , τ_1^{725} , and τ_2^{725} are lifetime components (and relative amplitudes) for lifetimes at 595 and 725 nm. Short lifetime components at 725 nm, τ_1^{725} , can be attributed to monomer emissions overlapped at the measured wavelength.

Empirical formula	$C_{46}H_{16}CI_{16}F_{12}N_2O_4Zn$	
<i>Fw</i> / g mol ⁻¹	1521.18	
Crystal system	Triclinic	
Space group	<i>P</i> -1	
Crystal size / mm	0.20×0.03×0.03	
Temperature / K	123	
<i>a</i> / Å	8.9829(6)	
b/Å	15.1174(8)	
c / Å	20.8813(7)	
lpha / °	97.411(4)	
βl°	94.728(4)	
γl°	90.909(5)	
V / Å ³	2801.4(3)	
$ ho_{ m calced}$ / g cm ⁻³	1.803	
λ/Å	0.71073	
μ / mm ⁻¹	1.288	
Reflection collected	34662	
Independent reflections	12845	
Parameters	809	
R _{int}	0.0519	
R_{1}^{a}	0.0792	
$wR_{2^{b}}$	0.2601	
GoF°	1.090	

Table S2 Crystallographic data of $Zn^{II}(hfac)_2(\alpha H-PyBTM)_2$

 $\label{eq:rescaled_states} \begin{tabular}{l} $^aR_1 = \Sigma ||F^o| - |F^c|| / \Sigma |F^o| \ (I \geq 2\sigma(I)). $^bwR_2 = [\Sigma(w(F^{o2} - F^{c2})^2 / \Sigma w(F^{o2})^2]^{1/2} \ (I \geq 2\sigma(I)). $^cGoF = [\Sigma(w(F^{o2} - F^{c2})^2 / \Sigma (N^r - N^p)^2]. $ \end{tabular}$



Fig. S3. Powder X-ray diffraction patterns of **PyZn_R**.



Fig. S4. Excitation spectra of PyZn_10 recorded at the emission wavelength of 595 and 725 nm.



Fig. S5. Emission spectra of $Zn^{II}(hfac)_2(PyBTM)_2$ and PyBTM grinded with αH -PyBTM. The emission of $Zn^{II}(hfac)_2(PyBTM)_2$ may result from free PyBTM dissociated by grinding.



Fig. S6. Emission decays and corresponding fitted curves of **PyZn_R** at (a)(b) 595 and (c) 725 nm and (d) those of **PyZn_10** at 900 nm.



Fig. S7. Intensity changes of (a) **PyZn_5** and (b) **PyZn_20** at monomer (λ_{em} = 595 nm) and excimer (λ_{em} = 740 nm) emission wavelengths at 4.2 K under a magnetic field. Monomer enhancement and excimer suppression indicate the increase in monomer intensity and the decrease in excimer emission intensity from intensities at 0 T, respectively.



Fig. S8. Proposed monomer species, magnetic field-sensitive process, and excimer species in **PyZn_R**.



Fig. S9. ¹H NMR spectrum of Zn^{II}(hfac)₂(αH-PyBTM)₂ (400 MHz, CDCI₃).



Fig. S10. ¹³C NMR spectrum of $Zn^{II}(hfac)_2(\alpha H-PyBTM)_2$ (100 MHz, CDCI₃).

References

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