Inorganic Chemistry

Bis(dipyrrinato)zinc(II) Complexes: Emission in the Solid State

Mizuho Tsuchiya,[†] Ryota Sakamoto,^{*,†,‡} Masaki Shimada,[†] Yoshinori Yamanoi,[†] Yohei Hattori,[†] Kunihisa Sugimoto,[§] Eiji Nishibori,^{||} and Hiroshi Nishihara^{*,†}

[†]Department of Chemistry, Graduate School of Science, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-0033, Japan [‡]JST-PRESTO, 4-1-8 Honcho, Kawaguchi, Saitama 332-0012, Japan

[§]Japan Synchrotron Radiation Research Institute (JASRI), 1-1-1 Koto, Sayo-cho, Sayo-gun, Hyogo 679-5198, Japan

^{||}Division of Physics, Faculty of Pure and Applied Sciences, Tsukuba Research Center for Interdisciplinary Materials Science, and Center for Integrated Research in Fundamental Science and Engineering, University of Tsukuba, 1-1-1 Tennodai, Tsukuba, Ibaraki 305-8571, Japan

Supporting Information

ABSTRACT: This Communication reports the first observation of solid-state photoluminescence in bis-(dipyrrinato)zinc(II) complexes with various substituents. The report discusses the effect of their substituents on their crystal structures and spectroscopic properties. Their *meso*-aryl groups are revealed to play important roles in the spectroscopic properties in the solid state.

ipyrrins are a class of π -conjugated organic molecules with intense absorption in the visible region.¹ In addition, their pyrrolic nitrogen atoms provide coordinating ability, and thus these compounds are often dyes and ligands. Of the known dipyrrin-metal complexes, most are boron complexes (boron dipyrromethenes, or BODIPYs), which are frequently used as fluorescent dyes.^{2,3} Although dipyrrinato-metal complexes are generally nonemissive, exceptions include some dipyrrinato-zinc(II) complexes.^{1,4-6} Lindsey and colleagues reported that a structurally rigid bis(dipyrrinato)zinc(II) complex exhibits emission with a fluorescence quantum yield $(\Phi_{\rm F})$ of 0.36 in toluene.⁷ Later, we revealed that elaborate heteroleptic bis(dipyrrinato)zinc(II) complexes emit at Φ_{μ} of up to 0.76 in toluene, which are comparable to those of BODIPYs.⁸ Antina and colleagues also discovered that double-helical bis(dipyrrinato)zinc(II) complexes exhibit fluorescence with $\Phi_{\rm F}$ reaching 0.91 in cyclohexane.¹⁰ Thus, recent efforts have realized luminescent bis(dipyrrinato)zinc(II) complexes in solution. In sharp contrast, their luminescent property in the solid state has hardly been studied.¹¹ Here, we developed for the first time a series of luminescent bis(dipyrrinato)zinc(II) complexes in the solid state (Scheme 1), discussing the relationship between their luminescent property and crystal structures.

The bulkiness of the *meso*-aryl group of dipyrrin ligands proved to affect the emissive properties of dipyrrin complexes in solution.¹² In association with the previous knowledge, several types of dipyrrin ligand bearing bulky aryl groups were prepared here: *meso*-9-anthracenyl, and 4-*tert*-butylphenyl ligands **2aH**, **2bH**, **2cH**, **3bH**, and **3cH**. According to reported methods,^{8,9} new zinc complexes **2a₂Zn**, **2b₂Zn**, **2c₂Zn**, **3b₂Zn**, and **3c₂Zn** were prepared. Hereafter, the structures and luminescent Scheme 1. Synthesis of Homoleptic $\operatorname{Bis}(\operatorname{dipyrrinato})\operatorname{zinc}(\operatorname{II})$ $\operatorname{Complexes}^a$



"Ligand 2aH and its homoleptic complex $2a_2Zn$ are depicted as examples. The complexes investigated herein are $1a_2Zn$, $1c_2Zn$, $2a_2Zn$, $2b_2Zn$, $2c_2Zn$, $3b_2Zn$, and $3c_2Zn$.

properties of the five complexes were disclosed and discussed, together with those of $1a_2Zn$ and $1c_2Zn$ synthesized previously.⁸

The complexes' spectroscopic properties in solution are summarized in Table 1, and their absorption spectra are shown in Figure 1a. The regions of absorption maxima (488–511 nm), molar extinction coefficients $(1.2 \times 10^5 - 1.6 \times 10^5 \text{ M}^{-1} \text{ cm}^{-1})$, and emission wavelengths (510-558 nm) are typical of bis(dipyrrinato)zinc(II) complexes and are attributable to the ${}^{1}\pi - \pi^{*}$ transition of the dipyrrin core.⁸ For complexes 2a₂Zn-2c₂Zn, there is an additional absorption band around 370 nm, attributable to the ${}^{1}\pi - \pi^{*}$ transition of the anthracene subunit. The constant absorption and emission wavelengths suggest that the meso-aryl groups of the complexes have little effect on the ground and photoexcited electronic states of the dipyrrin subunit. However, the fluorescence quantum yields are strongly affected by the meso-aryl groups; the conformation of the mesoaryl group in the excited state greatly affects the accessibility of nonradiative decay pathways. 13 The 2.8–4.5 ns fluorescence lifetimes are comparable to those of reported structures.⁷

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Table	1.	Spectrosco	pic Pro	perties of	Homol	eptic	Bis(d	lipy	rrinato)zinc(II)	Compl	lexes in S	Solution	(Toluene) and in t	he So	olid	State
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		in t	oluene solut	tion		in the solid state						
	λ_{abs}^{a}/nm	$10^{-5} \varepsilon^{b} / M^{-1} cm^{-1}$	$\lambda_{\rm exc}^{\ \ c}/{\rm nm}$	$\lambda_{\rm em}^{\ \ d}/{\rm nm}$	Φ_{F}^{e}	τ^{f}/ns	$\lambda_{abs}^{a,g}/nm$	$\lambda_{\rm exc}^{\ \ c}/{\rm nm}$	$\lambda_{\rm em}^{\ \ d}/{\rm nm}$	Φ_{F}^{e}	$\tau_1(f_1), \tau_2(f_2)^f/ns$	
$1a_2Zn$	495 ^h	1.6 ^h	495 ^h	509 ^h	0.20 ^h	4.5	519	500	615	0.02	0.64 (65%), 2.0 (35%)	
$1c_2Zn$	508 ^h	1.4 ^h	508 ^h	532 ^h	0.20 ^h	2.4	530	510	575	< 0.01		
$2a_2Zn$	498	1.39	484	513	0.090	2.8	528	510	635	0.03	0.43 (57%), 1.0 (43%)	
$2b_2Zn$	493	1.45	480	519	< 0.01		517	510	609	< 0.01		
$2c_2Zn$	511	1.29	496	558	< 0.01		526	510	581	0.01		
$3b_2Zn$	488	1.39	470	510	< 0.01	4.5	511	470	560	0.03	0.088 (71%), 1.1 (29%)	
3c ₂ Zn	506	1.21	490	538	< 0.01		521	510	608	<0.01		

^{*a*}Absorption maximum wavelength. ^{*b*}Maximum molar absorptivity. ^{*c*}Excitation wavelength. ^{*d*}Fluorescence maximum wavelength. ^{*e*}Fluorescence quantum yield. ^{*f*}Fluorescence lifetime excited at 470 nm. ^{*g*}measured as drop-cast thin film. ^{*h*}from ref 8.



Figure 1. Spectroscopic properties of complexes $1a_2Zn$ (orange dashed line), $1c_2Zn$ (light-blue dashed line), $2a_2Zn$ (red solid line), $2b_2Zn$ (green solid line), $2c_2Zn$ (blue solid line), $3b_2Zn$ (light-green dotted line), and $3c_2Zn$ (purple dotted line): (a) absorption and (b) emission in toluene and (c) emission in the solid state.



Figure 2. Crystal structures of (a) $1a_2Zn$, (b) $2a_2Zn \cdot 3CH_2Cl_2$, and (d) $3b_2Zn$ (thermal ellipsoids set at 50% probability). Hydrogen atoms and solvent molecules are omitted for clarity. These three structures, whose fluorescence quantum yields are above 0.01, are shown as representative structures. Color code: C, gray; N, purple; Zn, red.

Solid thin films of the complexes show absorption spectra reminiscent of those in solution, with 15-30 nm red shifts and broadened profiles compared with the complexes (Figure S1). These differences can be ascribed to the stronger intermolecular interactions in the solid. The seven complexes appear to be fluorescent in the solid state, and three of them had $\Phi_{\rm F}$ values above 0.01. The fluorescence properties in the solid state are distinctly different from those in solution (Table 1 and Figure 1), with each complex showing different emission wavelengths and spectra dependent on their crystal packing structure. The emission wavelengths are red-shifted compared with those in solution, and the spectra are broadened. 1a₂Zn emits at 615 nm with a $\Phi_{\rm F}$ value of 0.02; the fluorescence shows a dualexponential decay with lifetimes of 0.64 ns (65%) and 2.0 ns (35%). Similarly, 2a₂Zn emits at a more red-shifted wavelength, 635 nm, with a $\Phi_{\rm F}$ value of 0.03 and lifetimes of 0.43 ns (57%) and 1.0 ns (43%). 3b₂Zn fluoresces at 560 nm, close to its solution fluorescence wavelength (510 nm); its $\Phi_{\rm F}$ value is 0.03, and its lifetimes are 0.088 ns (71%) and 1.1 ns (29%). The series of dual emission should stem from two or more dipyrrinato

ligands in different chemical atmospheres in the crystal phase (vide infra). Given that the emission wavelengths, fluorescence quantum yields, and lifetimes in the solid state are entirely different from those in solution, the photophysics of the dipyrrinato-zinc complexes must also be substantially different in the solid state.

The single-crystal X-ray structures of the complexes were also studied (Figures S2–S8 and Tables S1–S7). Thermal ellipsoid plots and packing structures for $1a_2Zn$, $2a_2Zn$ ·3CH₂Cl₂, and $3b_2Zn$, which showed brighter solid-state luminescence than the others, are shown in Figure 2. $1a_2Zn$, a structure previously reported by our group,⁸ has Zn–N distances of 1.976–1.984 Å. The dihedral angle between the mean plane of the dipyrrin subunit and that of the mesitylene subunit is 84.4°. The two dipyrrin subunits coordinating to the zinc center also show an orthogonal conformation—the dihedral angle is 89.9° showing that the zinc center adopts a tetrahedral coordination sphere. Figure S9 shows a relative configuration between two dipyrrinato ligands in proximity to each other. The two dipyrrins has a head-to-tail orientation, with an offset distance of 3.199 Å. In this scheme, the transition dipole moment of the S_0-S_1 transition of the dipyrrin ligand also possesses a head-to-tail orientation, because it is propagated along the long axis of dipyrrin.¹² Therefore, the red-shifted solid-state emission in 1a₂Zn can be ascribed to exciton coupling.¹³ The single-crystal structure of 2a₂Zn·3CH₂Cl₂ shows characteristics similar to those of 1a₂Zn: the Zn-N distances are 1.959-1.990 Å, the dihedral angle between the anthracene and dipyrrin subunits is 84.3°, and the dihedral angle between the dipyrrin subunits coordinating to the zinc center is 88.9°. In addition to the features shared with $1a_2Zn_1$, intermolecular CH- π interaction between the anthracene moieties (\sim 3.0 Å) and the dipyrrin moieties (~2.8 Å) is observed in $2a_2Zn \cdot 3CH_2Cl_2$, and the interaction contributes to the ordered alignment of the molecules. 2a₂Zn·3CH₂Cl₂ also exhibits a dipyrrin-dipyrrin configuration similar to that of $1a_2Zn$ (Figure S10): the two dipyrrins has a head-to-tail orientation, with an offset distance of 3.214 Å. This structural feature may account for the red-shifted solid-state emission. However, the crystal and packing structures of $3b_2Zn$ are totally different from those of $1a_2Zn$ and $2a_2Zn$. 3CH₂Cl₂. Despite 3b₂Zn showing typical Zn-N distances of 1.977-1.983 Å, its 60.1° dihedral angle between the 4-tertbutylphenyl and dipyrrin subunits and its 78.9° angle between the dipyrrin subunits are distorted relative to those of 1a₂Zn and $2a_2Zn$, which can be attributed to a tighter packing structure.¹⁴ Figure S11 displays a relative configuration between two dipyrrinato ligands. The configuration is between the parallel and head-to-tail ones, and an offset distance of 4.190 Å is much further than those in $1a_2Zn$ and $2a_2Zn \cdot 3CH_2Cl_2$. This may explain the relatively small red shift of the solid-state luminescence in 3b₂Zn.

Thermogravimetric analysis revealed $2a_2Zn$ to be thermally stable below 380 °C (Figure S12). Therefore, a $2a_2Zn$ thin film was fabricated on a quartz substrate by vacuum deposition. The resulting UV–vis absorption and emission spectra are given in Figure 3. The absorption spectrum shows a maximum at 526 nm,



Figure 3. Absorption (red solid line) and emission (red dashed line, excited at 490 nm) spectra of a thin film of $2a_2Zn$ on quartz.

attributed to the ${}^{1}\pi - \pi$ transition of the dipyrrin subunit. Although the spectrum is red-shifted compared with that in solution (498 nm), it retains the characteristics observed in solution and is close to that in its thin film, whose maximum is at 528 nm. The emission spectrum exhibits a maximum at 626 nm, which is close to the maximum observed in the solid state (635 nm). The absorption and emission wavelengths suggest that the vacuum-deposited thin film contains aggregated states similar to those found in the drop-cast thin film or in the solid state.

In conclusion, we developed a series of solid-state emissive homoleptic bis(dipyrrinato)zinc(II) complexes and studied their spectroscopic properties and single-crystal X-ray structures. The great differences between the emission properties of the complexes in the solid state and in solution are ascribed to their aggregation states. This is the first report to study the solid-state emission of bis(dipyrrinato)zinc(II) complexes in depth. It will contribute to the understanding, design, and further study of bis(dipyrrinato)zinc(II) complexes.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorg-chem.6b00431.

Detailed synthetic and measurement procedures, UV-vis absorption spectra of thin films, X-ray crystallographic data, orientations of a pair of dipyrrinato ligands in the crystal phase, and thermogravimetric analysis (PDF) CIF file (CIF)

AUTHOR INFORMATION

Corresponding Authors

*E-mail: sakamoto@chem.s.u-tokyo.ac.jp.

*E-mail: nisihara@chem.s.u-tokyo.ac.jp.

Notes

The authors declare no competing financial interest.

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