

論文内容の要旨

論文題目 Exploration of Luminescent Dipyrin Complexes and Their Assemblies: Molecular Design, Synthesis, and Photophysics

(発光性ジピリン錯体とその集積体の探索：
分子設計、合成および光物性)

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Introduction

Dipyrins, or dipyrromethenes, are a group of fully π -conjugated molecules whose structures are comprised of two pyrrole rings. They are featured by intense absorption derived from the $^1\pi\text{-}\pi^*$ transition in the visible region ($\lambda_{\text{max}} \sim 500 \text{ nm}$, $\epsilon_{\text{max}} \sim 10^5 \text{ M}^{-1}\text{cm}^{-1}$).

They show affinity to various cations, resulting in various complexes (Figure 1). Although most of such complexes are non-fluorescent, there are a few exceptions; boron and zinc complexes are the most widely known fluorescent dipyrin complexes. Dipyrins' boron complexes, often abbreviated as BODIPYs (*boron-dipyrromethenes*), show intense fluorescence, whose quantum yields are close to unity even in polar solvent. In addition, they are featured by chemical and photochemical robustness and the manifold of chemical modification methods to tune their photophysical properties. Owing to the versatility, they are often utilized as fluorescent dyes, laser dyes, sensors, labels, etc. Dipyrinatozinc(II) complexes are also known to fluoresce as intense as BODIPYs under appropriate molecular designs. Since one zinc ion can accept two dipyrinato ligands, supramolecules and coordination polymers can be obtained, bound with photofunctionalities derived from the intrinsic photo properties of dipyrins. In my Ph.D. study, in exploration of the chemistry and photophysics of dipyrin complexes, two new series of dipyrinato complexes were developed and their photophysical properties were investigated.

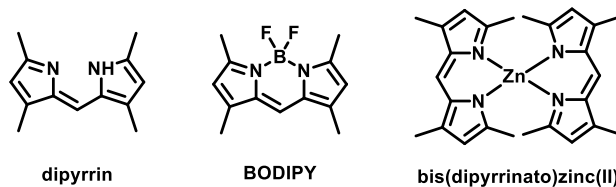


Figure 1. Structure of dipyrin and its complexes.

Photochemical Properties of BODIPY-imine Hybrids

An imine is an organic compound bearing a C=N bond. They are synthesized from aldehydes and amines, which react under mild conditions. The facile fabrication conditions are favorable in connecting multiple functional units to realize novel and intricate molecules and systems. There have been only a few reports on imine-BODIPY hybrids, though they are

weakly or non-fluorescent, spoiling BODIPYs' utility as fluorophores. In this research, development of fluorescent BODIPY-imine hybrids is pursued and their photochemical properties are investigated. BODIPYs with formyl group(s) at the 2- (and 6-) positions, **2** and **3**, are synthesized from BODIPY **1**, featured by fluorescence quantum yields (Φ_F) close to unity. They were reacted with either of 1,4-phenylene diamine, ethylene diamine, 1,12-dodecanediamine, or hydrazine monohydrate to prepare BODIPY-imine dimers and oligomers to investigate the effect of the bridging amines on their photophysical properties (Figure 2). The reactions proceeded in dichloromethane in ambient conditions without a catalyst and completed after stirred overnight. The 1,4-phenylenediamine-linked BODIPYs showed a distorted absorption spectrum and very weak fluorescence, due to a non-emissive photo-induced electron transfer process from the phenylene diamine subunit to the BODIPY core. The alkyldiamine-bridged BODIPYs, **5a**, **5b**, **6a**, and **6b**, exhibited intense emission ($\Phi_F = 0.87 - 0.93$) since the quenching process is absent. Their minimal spectral red-shifts ($\lambda_{em} = 521 - 558$ nm) from BODIPYs **2** and **3** ($\lambda_{em} = 512$ nm and 520 nm) suggest that there is little change in the electronic structure of the BODIPY core upon the formation of imine bonds. In sharp contrast to the alkyldiamine-bridged oligomers, the hydrazine-bridged oligomers **7a** and **7b** showed red-shifted emission spectra, up to a shift of 120 nm. For **7b**, all oligomeric species, from the dimer to hexamer, were separated, and their red-shifts of the absorption and emission wavelengths increased with the number of BODIPY units in the molecules ($\lambda_{em} = 570$ nm – 640 nm). Their spectral shape and fluorescence lifetimes ($\tau = 1.1 - 1.5$ ns) are significantly different from those of the alkyldiamine-bridged BODIPYs, attributed to their extended π -conjugation through the hydrazine bridge. Their fluorescence quantum yields are 0.39 to 0.67, can be considered as moderately emissive.

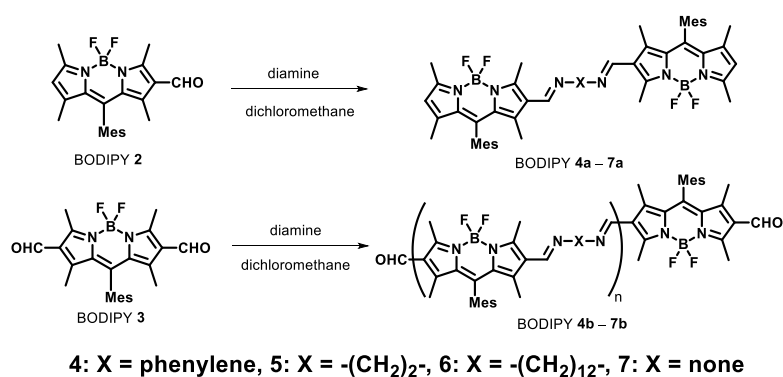


Figure 2. Synthesis of BODIPY-imine hybrids.

In this project, the synthesis of BODIPY-imine oligomers is reported and their photophysical properties are revealed. Their synthesis proceeds under mild conditions, without a catalyst. Spectroscopic analysis on the oligomers has disclosed that their photophysical properties depend on the type of the linker diamine used; while the alkyldiamine-linked oligomers achieve fluorescence quantum yields up to unity, the hydrazine-linked oligomers absorb and fluoresce at red-shifted wavelengths due to π -expansion. The facile synthetic methods and favorable fluorescent properties combine to render BODIPY-imine hybrids as versatile fluorescent materials.

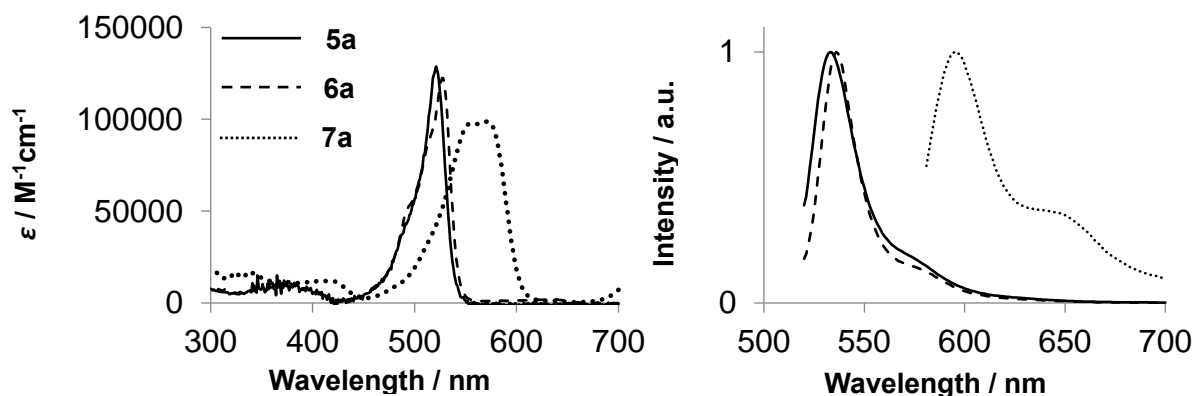


Figure 3. Absorption (left) and fluorescence (right) spectra of selected BODIPY-imine dimers **5a**, **6a**, and **7a**.

Solid-state Fluorescence of Homoleptic Bis(dipyrrinato)zinc(II) Complexes

Our group has investigated dipyrrins' another fluorescent group of compounds, bis(dipyrrinato)zinc(II) complexes. Our group has achieved high fluorescence quantum yields up to 0.78 (toluene) by carefully designing the electronic structure of the dipyrrinato ligands. Although bis(dipyrrinato)zinc(II) complexes are known to be fluorescent in solution, their fluorescence in the solid state has been unknown to date; fluorescence in the solid state would extend applications such as photoelectric conversion and OLEDs. This project focused to explore the solid state fluorescence of bis(dipyrrinato)zinc(II) complexes. Since bulky peripheral groups are known to affect the packing structure thus the emission properties of the resultant crystals, seven types of homoleptic bis(dipyrrinato)zinc(II) complexes with different peripheral groups were prepared (Figure 4). Either of mesityl, 9-anthracenyl, or 4-*tert*-butylphenyl group was introduced on the *meso*-position of dipyrrins as a bulky functional group to affect the alignment of the molecules in the solid state. Since alkyl groups on the dipyrrin moiety also affect the emission properties, either of 3,5-dimethyl, 1,3,5,7-tetramethyl, or 1,3,5,7-tetramethyl-2,6-diethyl group was introduced on the dipyrrin moiety. In toluene solution, the absorption and emission wavelengths ($\lambda_{\text{abs}} = 493 - 511$ nm, $\lambda_{\text{em}} = 509 - 558$ nm) are close to each other, showing the presence

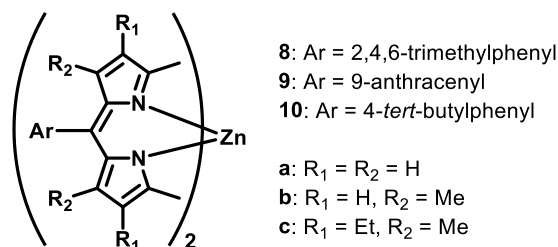


Figure 4. Bis(dipyrrinato)zinc(II) Complexes

of minimal electronic interactions between the *meso*-aryl group and dipyrrin core. On the contrary, their emission wavelengths are entirely different from those in solution ($\lambda_{\text{em}} = 560 - 635$ nm), and very different

from each other, reflecting the difference of peripheral groups on the molecules. Single crystal X-ray structural analysis revealed their crystal packing structure; dipyrin-dipyrin distances play important roles in the alignment of the molecules in the crystal packing structure. An anthracene bearing complex **9a** ($9a \cdot 3CH_2Cl_2$) showed the most red-shifted emission spectrum (635 nm), whose dipyrin-dipyrin distance is as short as 2.871 Å (Figure 5). The proximity enables the

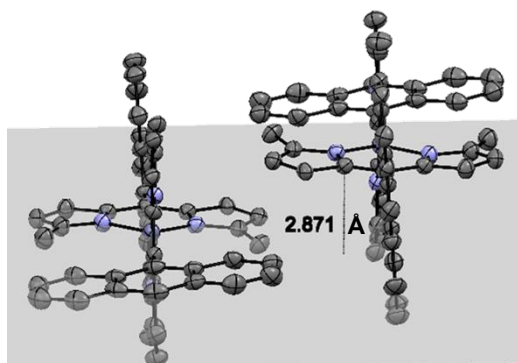


Figure 5. Packing structure of complex **9a**· $3CH_2Cl_2$. The dipyrin-dipyrin distance is shown in the figure.

dipyrin cores to induce excitonic coupling, accountable for the red-shifted emission wavelength. On the other hand, **10b** showed further dipyrin-dipyrin distance (4.190 Å), reflected in the modest red-shift of its emission wavelength (560 nm).

In conclusion, seven types of dipyrin zinc complexes were newly synthesized and their spectroscopic properties were revealed. The seven complexes are demonstrated to be fluorescent both in solution and in the solid state. Although the electronic structures of the seven complexes are similar to each other, their solid-state fluorescence is totally different; crystal packing structure is responsible for the wide range of emission wavelengths.

Conclusion

Through the two projects described, I have developed several new series of dipyrinato complexes. The new complexes were demonstrated to be fluorescent. The photophysics of the new complexes were investigated and their properties in regard their chemical structures were discussed.