論文の内容の要旨

論文題目 Development of New π-Conjugated Dipyrrin Complexes and Insight into Their Photochemical Processes
(新規π共役ジピリン錯体の開発および光化学過程の考察)

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Introduction

Dipyrrin is a monovalent bidentate ligand with two pyrrole groups, a substructure of porphyrin. Dipyrrin is very famous for its BF$_2$ complex (BODIPY), which shows strong light absorption at visible region and high fluorescence quantum yield, and it is intensely studied as light-harvesting antennas, bioprobes, laser dyes, and so on. Dipyrrin can also coordinate to various metal ions to form bis- or tris(dipyrrinato)metal complexes, and some of them such as Zn(II), Cu(II), Al(III), Ga(III) complexes are also known to show fluorescence. Such metal complexes are useful not only for pigment, but also supramolecular linker units, so that metal complexes are advantageous over BODIPYs in this regard. To focus on the fluorescence property, Zn(II) complexes are known to the highest ϕ_F among metal complexes. In my Ph. D. work, I studied syntheses of some BODIPYs and bis(dipyrrinato)Zn(II) complexes and their physical properties. Also, through the study of various complexes, I revealed the detailed photochemical processes, which is essential to utilize them as fluorescent materials.

Meso-alkynyl BODIPYs

Many BODIPYs with π-conjugated substituents have been reported, for example, alkynyl groups at 2,6- positions, and/or vinyl groups at 3,5- or 1,7- positions. However, there are only a few examples for substitution of a π-conjugated functional group such as alkynyl and vinyl groups at the *meso*- (8-) position. In order to reveal the detailed properties of *meso*- alkynyl substituted BODIPYs, I synthesized BODIPY monomers **1** and dimers **2** (Figure 1).

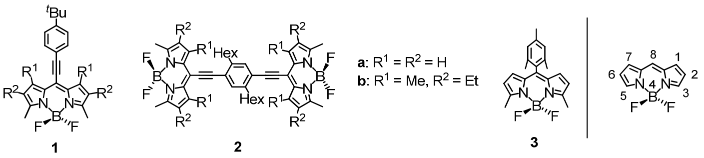


Figure 1. Novel *meso*-alkynyl BODIPYs **1** and **2**

UV-visible absorption spectra of **1a** showed a peak at 554 nm in hexane, which is red-shifted about 40 nm compared to the reference BODIPY **3a** (Figure 2). Fluorescence of **1a** was observed at 570 nm with high fluorescence quantum yield (ϕ_F = 0.86) in toluene. Generally, ϕ_F of BODIPY diminishes when a rotatable aryl group was introduced to the *meso*- position because of thermal rotation deactivation; however, high ϕ_F of **1a** showed no such influence of the phenylethynyl group.

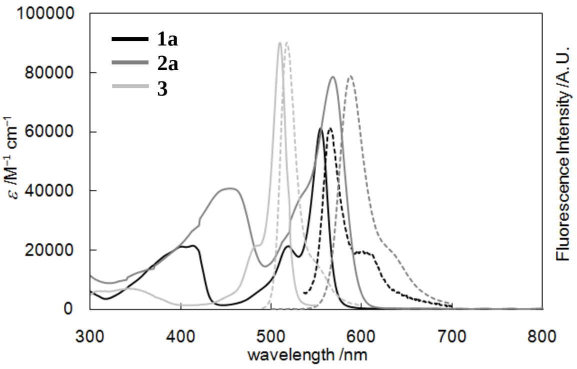


Figure 2. Absorption and emission spectra for **1a, 2a** and **3**

DFT calculation of **1a** showed that HOMO was completely localized on the dipyrrinato ligand, while LUMO was distributed around both the dipyrrinato ligand and the phenylethynyl group. As a result, the energy level of HOMO did not change from that of **3a**, while LUMO was lower reflecting the extension of π-conjugation. This behavior was also revealed by cyclic voltammetry: the oxidation potentials of **1a** and **3a** were almost identical (~0.9 V), while the reduction potential of **1a** (–1.21 V) was positively shifted than that of **3a** (–1.57 V).

Chapter 3. Heteroleptic Bis(dipyrrinato)Zn(II) Complexes

As mentioned before, Zn(II) complex is the most fluorescent among bis or tris(dipyrrinato)metal complexes, but the highest reported value was 0.36, far inferior to that of BODIPY which sometimes reaches almost 1.0. Meanwhile, mono(dipyrrinato)Zn(II) shows high ϕ_F, indicating that the effect of zinc atom, such as heavy atom effect, is not the major reason of low ϕ_F. This disadvantage has degraded bis(dipyrrinato)Zn(II) complexes as a fluorescence material.

In this work, I developed the charge-transfer hypothesis for fluorescence quenching in bis(dipyrrinato)Zn(II) complexes. The concise expression is as follows: photoexcitation of bis(dipyrrinato)Zn(II) complexes gave $^1\pi$-π^* excited state, in which one electron moves from one ligand to the other, to form charge-separated states (CS). $^1\pi$-π^* excited state and CS are in equilibrium and decay from $^1\pi$-π^* excited state accompanies fluorescence, while decay from CS goes thermally. As a result, the degree of contribution of $^1\pi$-π^* excited state determines the ϕ_F.

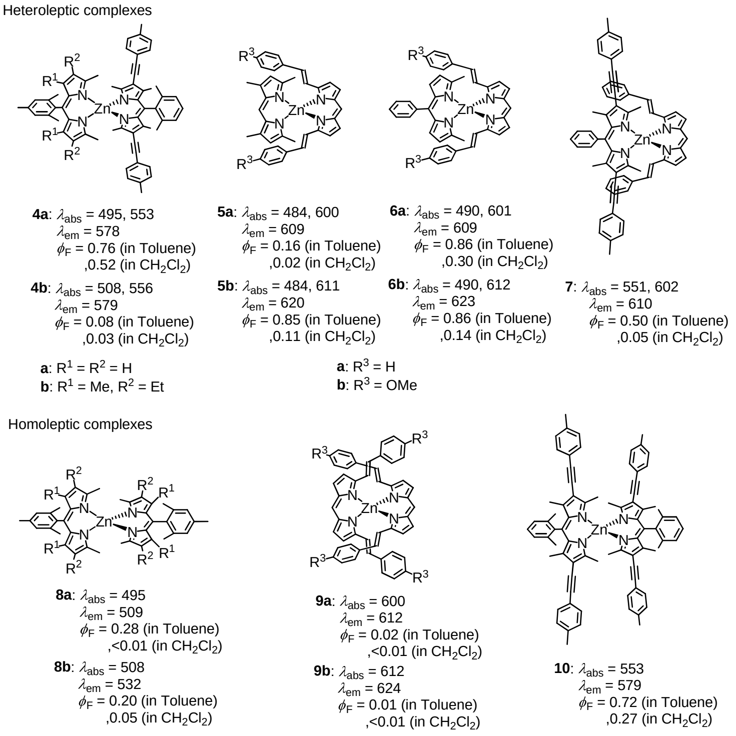


Figure 3. Heteroleptic and homoleptic bis(dipyrrinato)Zn(II) complexes

Based on this hypothesis, I developed heteroleptic bis(dipyrrinato)Zn(II) complexes for the purpose of the improvement of ϕ_F of bis(dipyrrinato)Zn(II) complexes. All heteroleptic complexes **4-7** were synthesized from the corresponding dipyrrinato ligands and zinc acetate (Figure 3). The structures were determined by X-ray crystallographic analysis. Although Zn(II) is known to be highly substitution active, heteroleptic complexes are stable in solution: heating a $CDCl_3$ solution of **4a** resulted in neither decomposition nor disproportionation.

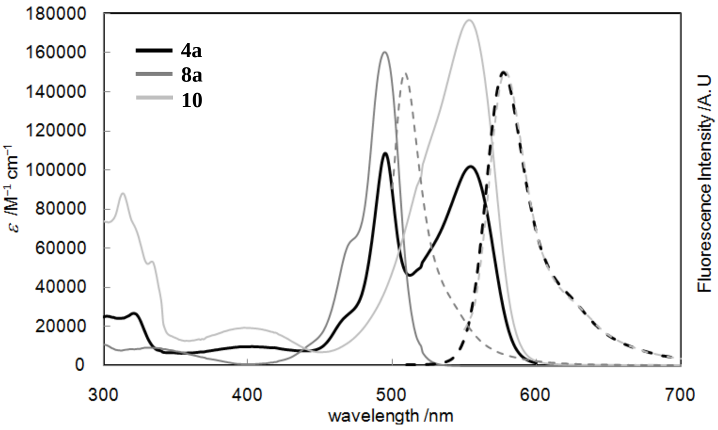


Figure 4. Absorption and emission spectra for **4a**, **8a** and **10**

UV-visible absorption spectra for heteroleptic complexes showed two absorption peaks corresponding to the π-π* transition of each ligands, and no shift from the absorption maxima of the corresponding homoleptic complexes. On the other hand, fluorescence spectra showed only one peak derived from the ligand with lower excitation energy (Figure 4). Excitation spectra for the most of heteroleptic complexes were revealed to be identical with their absorption spectra, indicating that when the ligand with shorter absorption wavelength was excited, the excitation energy was quantitatively transferred from this ligand to the other. The ϕ_F of heteroleptic complexes showed higher values than those of the corresponding homoleptic complexes except **4b**. Especially, ϕ_F of **4a**, **5b**, and **6** reached to the comparative value of those of the corresponding BODIPYs. On the other hand, **4b** showed very weak fluorescence.

As a representative of heteroleptic complexes **4-7**, the increase and decrease of ϕ_F in **4a** and **4b** are explained by charge-transfer hypothesis as described below (Figure 5). DFT calculation revealed that homoleptic complexes have two degenerated HOMOs and LUMOs assignable to the π and π* orbitals of dipyrrin ring. In heteroleptic complex **4a**, the HOMO and the LUMO localized on the π-conjugated dipyrrin ligand, and HOMO–1 and LUMO+1 localized on the companion ligand. On the other hand, HOMO and HOMO–1 of **4b** were reversed compared to **4a** because of the introduction of electron donating alkyl groups into the companion ligand. In heteroleptic complex **4a**, CS became unstable than homoleptic complex **10**, because of the energy difference between HOMO and HOMO–1, or LUMO and LUMO+1, which resulted in the increment of contribution of π-π* excited state and higher ϕ_F. In contrast, reversed ordering of HOMO and HOMO–1 in **4b** resulted in stabilization of the CS and in weak fluorescence.

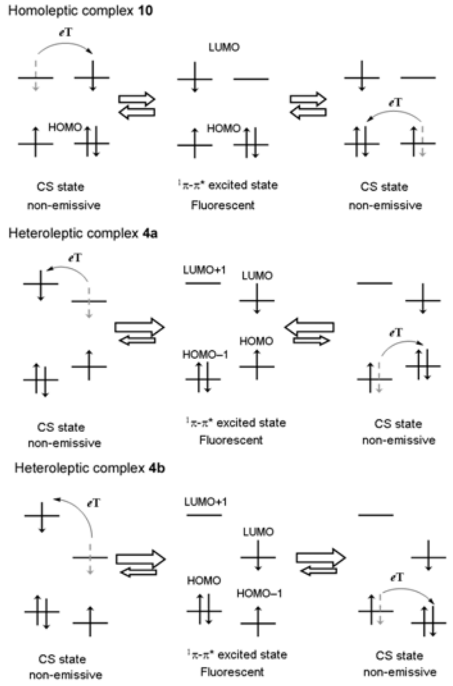
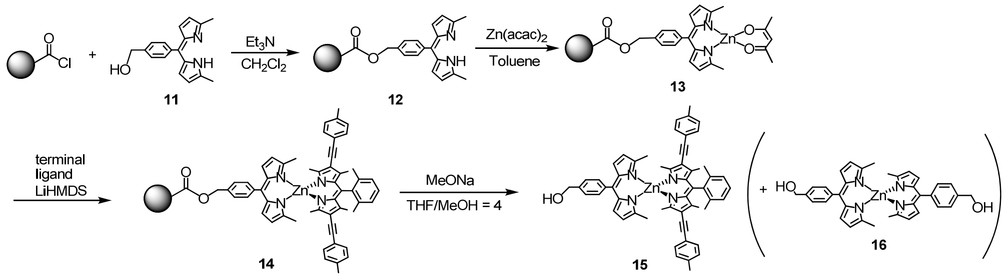


Figure 5. Illustration of charge-separation hypothesis

The existence of CS was suggested by other experimental results. All bis(dipyrrinato)Zn(II) complexes largely degrade their ϕ_F in more polar CH_2Cl_2 in which charge-separated states are generally more stabilized than in toluene: such tendency is not so evident in BODIPYs. It is worth noting that degradation in polar solvent is more evident in homoleptic complexes rather than heteroleptic ones, reflecting the efficient frontier orbital ordering. Moreover, direct observation of CS was attempted by time-resolved UV-visible absorption spectroscopy. Transient absorption spectrum for homoleptic complex **8a** showed the positive change at around 545 nm, which is assignable to the absorption peak of one electron oxidized and/or reduced product of **8a**.

I also studied solid-phase synthesis of heteroleptic bis(dipyrrinato)Zn(II) complexes, for reducing the generation of homoleptic complexes as the side product during the solution phase synthesis. Immobilization of a terminal ligand **11** to a polystyrene resin, subsequent coordination of a Zn(II) ion and another terminal ligand, and cleavage from the resin by saponification successfully gave heteroleptic complex **15**, although subgeneration of a homoleptic complex **16** could not be completely eliminated (Scheme 1).



Scheme 1. Solid-phase synthesis of a heteroleptic bis(dipyrrinato)Zn(II) complex

Heteroleptic Dipyrrin-Azadipyrrin Zn(II) Hybrid Complex

Azadipyrrin is another family of the dipyrrin, in which in which a methine carbon atom of dipyrrin at *meso*- position is substituted by a nitrogen atom. Azadipyrrin is also known to form a bis(azadipyrrinato)Zn(II) complex, however, all of them are reported to be non-fluorescent. I assumed that the fluorescence of bis(azadipyrrinato)Zn(II) complex quenches due to charge-separation pathway as shown in bis(dipyrrinato)Zn(II) complexes, and also I adopted the strategy used for bis(dipyrrinato)Zn(II) complexes into the azadipyrrin-Zn(II) complex. Heteroleptic azadipyrrin-Zn(II) complex **17** (Figure 6) bearing a π-conjugated azadipyrrinato ligand and a simple dipyrrinato ligand was synthesized by the same way as heteroleptic bis(dipyrrinato)Zn(II) complexes. The structure of **17** was revealed by X-ray crystallographic analysis and zinc center was distorted from tetrahedral because of π-π interaction between the phenyl group and the pyrrole ring. **17** showed sharp absorption band at 485 nm and 656 nm, and exhibited fluorescence exclusively at 672 nm. Although the fluorescence quantum yield was very low (ϕ_F = 0.00043), considering that the corresponding bis(azadipyrrinato)Zn(II) complex **18** was totally non-emissive, the result indicates the success of strategy for the improvement of the fluorescence quantum yield.

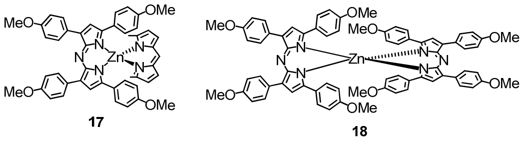


Figure 6. Heteroleptic and homoleptic azadipyrrinatoZn(II) complexes

Dipyrrin Zn(II) Complexes bearing Supporting Ligands

Chapter 3 showed the improvement of the fluorescence quantum yield of bis(dipyrrinato)Zn(II) complexes, however, this can adopt to the heteroleptic complexes bearing π-conjugated dipyrrin as a fluorescent ligand. Therefore, for the purpose to improve the fluorescence of the Zn(II) complexes with simple dipyrrin as fluorescent ligand, the use of a supporting ligand with shorter absorption wavelength than a dipyrrin was investigated. At first, a dipyrrinato Zn(II) complex **19** with an iminopyrrolyl supporting ligand was developed (Figure 7). **19** seemed to be highly fluorescent, however, this was unstable in solution and could not be isolated. Next, complex **20** bearing a bisoxazoline ligand was synthesized. **20** was highly fluorescent in solution (ϕ_F = 0.70 in toluene) and stable enough to be isolated. Considering that previously reported mono(dipyrrinato)Zn(II) complexes are usually highly unstable like **19**, development of **20** expands the potential use of dipyrrinatoZn(II) complexes as photochemical materials.

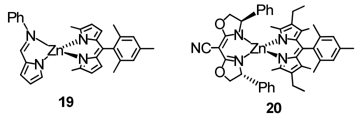


Figure 7. Fluorescent mono(dipyrrinato)Zn(II) complexes

Conclusion

In conclusion, new BODIPYs and dipyrrinatoZn(II) complexes were developed. Their photophysical properties were revealed along with electrochemical and theoretical studies. The charge-separation mechanism in the photochemical process of bis(dipyrrinato)Zn(II) complexes was proposed. The strategies for the improvement of the fluorescence quantum yields based on the hypothesis were successful, suggesting the reasonability of the existence of the charge-separated states. In addition, the direct observation of the charge-separated state proved the hypothesis.