Design and Synthesis of Dipyrin Complexes Bearing Unique Structures, Properties and Functions

Tatsuya Nabeshima^{1*}, Masaki Yamamura¹, Gary J. Richards², and Takashi Nakamura¹

¹*Graduate School of Pure and Applied Sciences and Tsukuba Research Center for Interdisciplinary Materials Science (TIMS), University of Tsukuba
1-1-1 Tennodai, Tsukuba, Ibaraki 305-8571, Japan*

²*Leading Graduate School Promotion Center, Ochanomizu University
2-1-1 Otsuka, Bunkyo-ku, Tokyo 112-8610*

(Received July 17, 2015; E-mail: nabesima@chem.tsukuba.ac.jp)

Abstract: We first describe N_2O_2 -type dipyrins, which behave as tridentate or tetradentate ligands for the preparation of main-group-element complexes including B, Al, Si, Ge, and Sn. Similar complexes were unstable or hard to prepare using usual bidentate dipyrins. In particular, the stable hypercoordinate dipyrin-silicon complexes showed interconvertible photo-optical properties. The Ge and Sn complexes were obtained in a similar way. *Ar,O*-BODIPYs were also synthesized from the N_2O_2 -type dipyrins. Their application to a light harvesting molecular assembly is also shown. Second, we demonstrate the usefulness and potential of dipyrin complexes in supramolecular chemistry. The one-, two- and three-dimensional supramolecular architectures are available because multidentate dipyrin derivatives can be easily obtained through chemical modifications of the dipyrin skeleton. Last we describe the binding ability of the fluorine atoms in BODIPY to cationic guests to create a functional response to an external stimulus.

1. Introduction

Dipyrin is nearly a half unit of porphyrins and works as a bidentate ligand to afford a variety of complexes with main group and transition elements.¹ In particular, its boron complex, BODIPY (4,4-difluoro-4-bora-3a,4a-diaza-*s*-indacene) is one of the most frequently used fluorophores because of its thermal and photostability and excellent photophysical properties such as sharp absorption and high fluorescence efficiency.² In addition, chemical modifications of BODIPY such as introducing substituents and expanding its π -system have often been carried out with the aim of tuning the photo-optical properties. Consequently, BODIPY derivatives have been applied for fluorescent labeling reagents, chemosensors, OLEDs, solar cells, laser dyes, electrogenerated chemiluminescence, bioimaging, *etc.* In contrast to the BODIPYs, highly fluorescent and functional dipyrin complexes with other elements are limited. This is probably because preparing such dipyrin complexes is sometimes more difficult than BODIPYs.

Despite the considerable versatility of BODIPYs, they have not often been utilized as building blocks for supramolecular architectures, although they are a partial unit of the porphy-

rins, which are very useful as building blocks. However, we are convinced that the BODIPYs could be incorporated into supramolecular frameworks to achieve sophisticated structures and photo functions. We also envisaged that BODIPYs worked not only as emissive units but also as recognition sites of host molecules to cationic guests (*vide infra*).

In this account we describe N_2O_2 -type dipyrins, which behave as a tridentate or tetradentate ligand for main-group-element complexes including B, Al, Si, Ge, Sn, *etc.* In addition, applications of the BODIPY units to rigid, flexible and responding supramolecular systems are demonstrated to emphasize the importance, usefulness and potentials of dipyrin complexes in supramolecular and materials chemistry.

2. N_2O_2 Dipyrin Complexes with Unique Structures and Functions

Although most BODIPYs are BF_2 complexes of dipyrin, a series of BODIPYs with different substitutions instead of the fluorine atoms on the boron centers have been reported.³ In particular, N_2O_2 -type tetradentate dipyrin ligands, which have two phenoxy groups at the 3,5-positions, afforded BODIPYs bearing one or two oxygen substitutions, which show interesting properties and functions. First N_2O_2 -type dipyrin and the corresponding BODIPY **1** were reported in 1999 with the aim of developing a novel fluorophore (Figure 2).⁴ The BODIPY **1** exhibited fluorescence at 654 nm with high quantum yield of 0.41. The fluorescence emission peak is significantly red-shifted (ca. 50 nm) compared to usual BODIPYs, BF_2 complexes of dipyrin. For the last decade, some studies focused on dyes and fluorophores that are based on N_2O_2 -BODIPYs. They show absorption and fluorescence in the red-to-NIR region. Uno *et al.* reported that N_2O_2 -BODIPYs **2** and **3** fused with aromatic rings exhibited fluorescence in a significantly red-shifted region.⁵ Kubo *et al.* also reported fused N_2O_2 -BODIPYs **4** and **5**. The BODIPY **5** was utilized as a

Figure 1. Dipyrin and BODIPY.

Figure 2. N_2O_2 -BODIPYs and their optical properties.

light harvester in heterojunction solar cell devices.⁶

The N_2O_2 -type dipyrins are useful not only for tuning the optical properties but also for the preparation of a variety of dipyrin complexes containing a central atom other than boron. In general, dipyrin complexes show intriguing functions based on the various coordination structures of the central element. The N_2O_2 -type dipyrin was expected to stabilize the complexes of typical elements by a chelate effect. Indeed, we synthesized the first stable dipyrin aluminum complexes using an N_2O_2 -type dipyrin ligand.⁷ We also obtained the silicon complexes of the N_2O_2 -type dipyrin due to the unique ligation environment.

The silicon complexes **7** were synthesized in moderate yields by the reactions of N_2O_2 -type dipyrin **6** with chlorosilanes in the presence of $NEt(iPr)_2$ (Table 1, entries 1–4).⁸ These are the first reported dipyrin silicon complexes. All the complexes **7** have a pentacoordinate silicon center (hypercoordinate structure), which includes one more substituent compared to the usual tetracoordinate silicon. X-ray crystallographic analysis of **7c** revealed that the silicon center adopted a trigonal-bipyramidal (TBP) geometry (Figure 3). Due to the TBP geometry, the dipyrin moiety is nonplanar. A silicon complex

Table 1. Synthesis of silicon, germanium, and tin complexes of N_2O_2 -type dipyrin.

entry	E	Ar	R		yield (%)
1	Si	Ph	Me	7a	46%
2	Si	Mes	Me	7b	47%
3	Si	Ph	Ph	7c	67%
4	Si	Mes	Ph	7d	40%
5	Ge	Ph	Ph	8	73%
6	Sn	Ph	Ph	9	80%

of a bidentate dipyrin was not obtained under the same reaction conditions. Hence, the chelate effect of an N_2O_2 -type dipyrin appears to play an important role in forming the stable hypercoordinate silicon complexes.

Figure 3. Molecular structures of (a) **7c** (E=Si), (b) **8** (E=Ge), and (c) **9** (E=Sn). Thermal ellipsoids set at 50% probability.

Fluorescence of the silicon complexes was observed between 648–662 nm. The quantum yields (Φ) of **7a** and **7c** having a *meso*-Ph group are low (0.012 for **7a** and 0.028 for **7c**) while those of **7b** and **7d** having a *meso*-Mes group are much higher (0.76 for **7b** and 0.72 for **7d**). These results indicate that the internal rotation of the Ar group causes an efficient nonradiative decay.⁹

The germanium and tin complexes **8** and **9** were synthesized in a similar way (Table 1, entries 5 and 6).¹⁰ X-ray crystallographic analysis of **8** revealed that the germanium center adopted a trigonal-bipyramidal (TBP) geometry similar to the silicon complex **7c** but the geometry of **8** ($\tau=0.67$) is more distorted from the ideal TBP structure than that of **7c** ($\tau=0.82$). In contrast, the tin complex **9** adopts a dimeric hexacoordinate structure.

The absorption maxima of **7c**, **8**, and **9** are observed at 612,

620, and 637 nm and fluorescence emission appears at 650, 675, and 664 nm in **7c**, **8**, and **9**, respectively. The Φ values are very different in **7c** (0.028), **8** (0.12), and **9** (0.22). The structural difference appears to affect the free rotation of the *meso*-Ph group to result in the Φ difference. Importantly, this study demonstrates that the photophysical properties of dipyrin complexes are tunable by changing the central atom.

Silanol **10** was obtained using a similar synthetic procedure to that for **7** (Scheme 1). Disiloxane **11** was accompanied but in very low yield (<1%). From X-ray crystallographic analysis, the two silicon atoms of **11** adopted a TBP geometry and the two dipyrin-complex moieties were connected by the μ -oxo oxygen located at the inversion center (Figure 4).

Scheme 1. Synthesis of silanol **10** and disiloxane **11**.

Figure 4. Molecular structure of **11**. Thermal ellipsoids set at 50% probability. Hydrogen atoms and solvent molecules are omitted for clarity.

The disiloxane **11** was hydrolyzed to **10** (**10**:**11**=95:5) by refluxing in wet MeOH (Scheme 2). On the other hand, the dehydration of **10** occurred by refluxing in hexane to reproduce **11** (**10**:**11**=10:90). The reversibility of the interconversion hydrolysis and dehydration is noteworthy because the usual tetracoordinate siloxanes resist hydrolysis. The facile hydrolysis of **11** is considered to be due to the properties of the hypercoordinate silicon complex.¹¹ Therefore, this interesting feature causes the reversible interconversion between the monomer and dimer of the dipyrin complexes. The monomer **10** showed sharp absorption and fluorescence at 605 and 629 nm, respectively. In contrast, the dimer **11** showed two absorption peaks

Scheme 2. Interconversion between **10** and **11**.

at 573 and 601 nm and fluorescence at 664–672 nm. In other words, the structural interconversion between the monomer **10** and dimer **11** regulates the optical properties.

Germoxane **12**, a germanium analog of the siloxane, was synthesized using a similar method to that of **11** (Scheme 3).¹² In the crystal structure, the Ge atoms of **12** have a slightly distorted TBP geometry (Figure 5). The structure of **12** is almost the same as that of **11** except the bond angle of Ge–O–Ge (120.62(11)°), which is much narrower than that of the Si–O–Si of **11** (180°).

Scheme 3. Synthesis of **12**.

Figure 5. Molecular structure of **12**. Thermal ellipsoids set at 50% probability. Hydrogen atoms and solvent molecules are omitted for clarity.

The recrystallization of **12** from methanol afforded the single crystal of monomer **13** having the hexacoordinate germanium center (Figure 6). It is interesting that the structure of the Ge analog **13** is different from that of the Si complexes.

Figure 6. Molecular structure of **13**. Thermal ellipsoids set at 50% probability.

The dimer **12** was immediately hydrolyzed in C_6D_6 or $CDCl_3$ to give monomer **14** (Scheme 4). The addition of DBU to **14** produced the dimer **15** in solution. Although all the coordinating ligands in **14** and **15** are not clarified in solution, the monomeric and the dimeric structures of **14** and **15** are

confirmed by DOSY spectra, respectively. The addition of AcOH to **15** reproduced **14**. This facile interconversion by the addition of base (DBU) and acid (AcOH) is superior to that of the silicon complexes, which is achieved by refluxing and solvent exchange. The fluorescence of **14** (669 nm) appeared at a slightly red-shifted region upon the addition of DBU because dimer **15** (674 nm) was formed.

Scheme 4. Interconversion between monomeric and dimeric germanium complexes.

Nozaki *et al.* reported dipyrin germanium and tin complexes in 2011.¹³ All of their complexes were isolated as monomers probably due to the steric effect of the bulky *tert*-butyl substituents on the dipyrin unit, which inhibits the dimerization (Figure 7). The monomeric germanium and tin complexes were utilized as a catalyst for polymerization of epoxides with carbon dioxide. In addition to the germanium and tin complexes, zirconium and titanium analogous of the N₂O₂-type dipyrin were also synthesized and utilized as catalysts for the copolymerization using tetravalent metal complexes as a main component of catalysts.

Figure 7. Tetravalent metal complexes of N₂O₂-type dipyrin utilized as a catalyst for polymerization of epoxides with carbon dioxide.

The central atom in the N₂O₂-dipyrin complex contributes to the unique complex structure and optical properties. In these complexes, the two oxygen atoms coordinate to the central atom. One more interesting complex available from the N₂O₂-type dipyrin and boronic acid is *Ar,O*-BODIPYs, which have an Ar group on the boron center (Scheme 5).¹⁴ The synthetic methods for preparation of BODIPYs having an Ar group on the boron had been limited to nucleophilic attack to the BF₂ unit with Grignard or organolithium reagents.¹⁵ However, these methods usually gave the desired product in low or moderate yields and laborious purification was often required. On the other hand, our method has significant advantages: no additives or no catalyst and high yield. The *Ar,O*-BODIPYs exhibited intense fluorescence at 613–615 nm. The emission wavelengths are in between of those of F-BODIPY (600 nm) and N₂O₂-BODIPY (645 nm)⁷ (Table 2). Interestingly, the flu-

Scheme 5. Synthesis of *Ar,O*-BODIPYs.

Table 2. Fluorescence properties of *Ar,O*-BODIPYs.

	Ar	R	λ_{em} / nm	Φ_{em}
16a	Ph	H	614	0.65
16b	1-Nap	H	615	0.68
16c	4-MeOC ₆ H ₄	H	613	0.63
17a	Ph	Me	644	0.59
17b	Ph	C ₄ H ₉	643	0.60
17c	Ph	Bn	642	0.62
F-BODIPY			600	0.88
N ₂ O ₂ -BODIPY			645	0.72

orescence wavelengths and quantum yields (0.63–0.68) are not affected by the Ar group at the boron center.

The residual phenol OH group of **16a** was alkylated to give **17a–c** (Scheme 6). The compounds **17a–c** exhibited a red-shifted fluorescence at 642–644 nm with quantum yields of 0.59–0.62 (Table 2). The alkylation is important for the red-shifted fluorescence but the alkyl group has almost no effect on the fluorescence efficiency.

Scheme 6. Synthesis of alkylated *Ar,O*-BODIPYs.

Alkylated *Ar,O*-BODIPY **17a** was hydrolyzed to give dipyrin ligand **18**¹⁶ having a methoxy group (Scheme 7). The reaction of **18** with boronic acid gave **19**, **20**, and **21**.¹⁷ *Ar,O*-BODIPY **19** having a pyrene unit exhibited only BODIPY flu-

Scheme 7. Synthesis of *Ar,O*-BODIPYs **19–21**.

orescence and no pyrene fluorescence was observed even when the pyrene unit was excited. This result indicates that excitation energy of the pyrene unit is transferred to the *Ar,O*-BODIPY unit via the Förster-type resonance energy transfer (FRET) mechanism (Table 3).

Table 3. Optical properties of *Ar,O*-BODIPYs **19–21** and the conjugate with **22**.

	λ_{em} / nm	Φ_{em}	FRET efficiency
19	650	0.56	> 99%
20	642	0.56	–
20·22	644	0.066	70%
21	643	0.59	–
21·22	644	0.55	99%
22	550	0.027	–

The reaction of *Ar,O*-BODIPY **20** with saloph·Zn complex **22** gave complex **20·22** in hexane (Scheme 8). The association constant (K_a) was determined by spectral titration to be $(7.3 \pm 2.3) \times 10^7 \text{ M}^{-1}$. The large value of K_a is indicative of the negligible dissociation process of the complex. The Zn complex **22** itself exhibited fluorescence at 550 nm while the complex **20·22** exhibited only BODIPY fluorescence because of FRET. Although FRET in **20·22** is efficient, the fluorescence quantum yield is very low (0.066). The stereoisomer **21·22** showed high FRET efficiency (99%) but the quantum yield is as high as 0.55. Thus, an appropriate arrangement of the energy donor and acceptor is necessary to construct the highly efficient FRET system.

Transition metal complexes of N_2O_2 -dipyrrin ligand, Cu,¹⁸

Scheme 8. Preparation of conjugate **20·22**.

Figure 8. (a) *Meso*-substituted dipyrrins commonly used to prepare a variety of coordination assemblies. (b) An example of 1-dimensional coordination polymer formation through reaction of **25** with copper acetylacetonate.

Mn,¹⁹ Co,^{20,21} and Ni²¹ were also reported. Although the emission properties of these complexes were not observed, they showed various intriguing properties, such as catalytic activity, redox activity, chiroptical properties, pharmaceutically relevant properties.

3. Applications of Dipyrrin Complexes to Supramolecular Chemistry

Molecular self-assembly and molecular recognition/host-guest chemistry are two of the most important concepts in supramolecular chemistry. Molecular self-assembly is the construction of systems often consisting of a large number of units held together through non-covalent interactions. Molecular recognition involves the specific binding of guest molecules to a complementary host to form a host-guest complex. In this section we deal with these two important concepts in relation to dipyrrins.

Non-covalent interactions have been utilized to form 1-dimensional, linear polymeric structures in a variety of dipyrrin-based systems.²² Most commonly, coordination polymers held together using ligand-metal interactions have been investigated with a view to realizing materials with novel optical, catalytic, magnetic and electronic properties.²³ *Meso*-substituted dipyrrin ligands have a rigid, easily derivatized structure that make them attractive targets for the preparation of coordination polymers. The dipyrrin moiety acts as a monoanionic ligand that forms stable complexes with a variety of transition metal cations. Commonly, the *meso* substituent contains a pyridine or quinoline function that can undergo secondary complexation to the metal center through distal nitrogen atom ligation. As well as polymerization through secondary complexation, hydrogen-bonding and other dipolar interactions have been utilized to stabilize 1-dimensional structures, thus compounds **23–28** (Figure 8) have been used as the dipyrrin unit in a variety of coordination assemblies.^{22,24}

Dipyrrins have been used in the construction of both 2-dimensional polymers and discrete molecular assemblies such as rings and sheets.^{24,25} Sheet-like structures are anticipated to produce novel catalytic, electronic and photonic materials.²⁶ Sakamoto and co-workers nicely illustrated how novel functions from nanosheets prepared using a bottom-up approach could be realized. Compound **29** produces multi-layer nanosheets using a liquid-liquid interfacial synthesis with

Figure 9. Compound **29** forms nanosheet structures upon complexation with Zn^{2+} ions.

Figure 10. Schematic illustration showing the synthesis of a pillared-paddlewheel type MOF through reaction of compounds **30** with zinc ions followed by reaction with **31**.

Figure 11. Self-assembled cyclic boron-dipyrrin oligomers.

Zn^{2+} ions or single-layer and few-layer nanosheets using a liquid–air interfacial reaction. Results showed that a photocurrent could be derived from the photocatalytic oxidation of triethanolamine sensitized by the nanosheets. Analogous compounds, which did not form self-assembled monolayers resulted in much lower conversion efficiencies, thereby justifying the superiority of the bottom-up nanosheet over conventional molecular films.²⁷

Coordination polymerization in three dimensions gives rise to a class of materials known as metal–organic-frameworks or MOFs. Three-dimensional MOFs can have a porous structure resulting in extremely large surface-areas and the choice of both metal and organic linker molecules has a significant effect on the structure and properties of each particular MOF. MOFs hold great promise for applications including gas storage and separation and catalysis among others.²⁸ Dipyrrins have been used as organic linker molecules for the construction of a variety of MOFs.²⁹ Hupp and co-workers prepared ‘pillared-paddlewheel’ type MOFs featuring BODIPY and porphyrin-based struts, capable of harvesting light across the entire visible spectrum. A symmetrical porphyrin strut **30** was chosen as the primary chromophore for the MOF synthesis together with a pyridine-functionalized BODIPY **31**. Together,

the two components were capable of collecting most of the light constituting the visible spectrum.³⁰

Dipyrrins-based molecular assemblies have been utilized as responsive host units in host–guest complexes. Host–guest complexation can cause a change in the photophysical properties of the dipyrrin unit and because of their large absorption and fluorescence in the visible range; such host–guest complexes can give rise to novel sensing properties.

Ikeda and Nabeshima prepared a series of cyclic boron-dipyrrin oligomers **33a–c** through reaction of dipyrrin catechol **32** and BCl_3 in refluxing toluene. A mixture of oligomers resulted, which could be separated using gel permeation chromatography. XRD analysis of oligomers **33a** and **33b** revealed triangular and square-prism structures composed of the dipyrrins, which were connected by the boron atom coordinated to the two pyrrolic nitrogens and the two catecholate oxygen atoms. In both cases, the inner catecholate oxygens form cavities with a radius of ~ 1.4 Å and ~ 2.7 Å for **33a** and **33b** respectively. The square-prism assemblies of **33b** stacked together to form one-dimensional channels, which are expected to be of interest in view of nano-porous materials. As the ~ 3 Å cavity of **33a** is surrounded by catecholate oxygen atoms as well as electron-rich pyrrolic planes, an interaction

with metal ions is expected. ^1H NMR spectroscopy showed no interaction with Na^+ ions, presumably because the ionic radius of Na^+ (0.97 Å) is smaller than the cavity radius (1.4 Å). However, K^+ , Rb^+ and Cs^+ caused considerable spectral changes indicating the formation of 1:1 complexes.^{3b}

Another means to produce a metal cation sensing effect in dipyrrrins is to append specific metal binding sites to the dipyr-rin unit. In particular, the fluorescence properties of the dipyr-rin unit can be strongly influenced when interaction with a metal cation causes a perturbation of intramolecular charge transfer processes in the dipyr-rin derivative. Richards and coworkers prepared a dithiacrown ether appended BODIPY compound **34**, which was capable of binding both Pb^{2+} and Hg^{2+} in the dithiacrown ether cavity.

Figure 12. Dithiacrown ether appended BODIPY, which acts as a switch-on fluorescence sensor for Hg^{2+} and Pb^{2+} ions.

In polar solvents, the bright red fluorescence of **34** is strongly quenched due to photoinduced electron transfer (PeT) from the benzo-dithiacrown ether moieties. However, binding of either Pb^{2+} or Hg^{2+} leads to an increase in the oxidation potential of the benzo-dithiacrown ether substituents and the PeT quenching mechanism is thus inhibited leading to a large increase in fluorescence. Thus **34** acted as a switch-on photoluminescence sensor for these highly toxic metal ions.³¹

The BODIPY and its analogs have often been used as reporting units for molecular recognition because of their excellent photophysical properties.^{1,2} On the other hand, the BODIPY derivatives had never been employed as binding sites for a guest. However, we conceived that the fluorine atoms of the BODIPY could effectively interact with a cationic guest because of the large difference in electronegativity between B (2.0) and F (4.0).³² The fluorine atom of a C–F bond are less polarized due to the smaller electronegativity of C (2.6)³² yet can still contribute to cation binding.³³ Therefore, electrostatic interaction of the BODIPY's fluorine atoms with such a guest should be stronger. In addition, an electrostatic potential map of BODIPY obtained by DFT calculation also indicates that the F atoms have partial negative charge (Figure 13) and are thus suitable for cation recognition via electrostatic interactions. In this context, the arrangement of multiple BODIPY units in ways where B–F bonds are appropriately accumulated were expected to enhance the recognition ability toward cationic guests via cooperative interaction with the fluorine atoms. To the best of our knowledge, there had been no attempts to utilize B–F bonds for molecular recognition before our reports described below.

Figure 13. A chemical structure and a negative electrostatic potential surface (–80 kJ/mol) obtained by DFT calculation (B3LYP/6–31G*) of 4,4-difluoro-4-bora-3a,4a-diaza-s-indacene (BODIPY).

A triangular macrocycle was designed by connecting three BODIPY units at their α -positions with *p*-phenylene linkers (Figure 14).³⁴ The synthesized macrocycle **35** has a planar structure with a 4-Å central cavity. The inner surface of the cavity was negatively charged because of the fluorine atoms. As a result, the macrocycle recognized the dibutyl ammonium cation within its cavity to form a pseudorotaxane, which was clarified by ^1H NMR, MALDI-TOF Mass, and X-ray crystallographic analysis.

Figure 14. (a) The chemical structure of **35**, a triangular macrocycle with three BODIPY units. (b) X-ray crystal structure of pseudorotaxane of BODIPY macrocycle **35** and a dibutyl ammonium cation. Hydrogen bonds between fluorine atoms of **35** and hydrogen atoms of the dibutyl ammonium cation are shown in dashed lines. Stick model. Phenyl groups in **35**, counter anions, and solvent molecules are omitted for clarity.

Intriguingly, linear BODIPY oligomers realized a larger change in absorption and fluorescence in response to cationic guests (Figure 15).³⁵ This was a result of a conformational change from open to folded form upon trapping of the guests. A series of BODIPY oligomers **36a–36e** were synthesized by condensation of bis(pyrrolyl)-2,5-dimethoxybenzene and 2,4,6-trimethylbenzaldehyde, followed by oxidation and reaction with boron trifluoride diethyl etherate. Extended oligomers **36c–36e** exhibited strong absorption and fluorescence in the red to near-infrared region ($\lambda \geq 650$ nm), which is an important property for applications such as bioimaging³⁶ and dye-sensitized solar cells.³⁷ Among them, the linear BODIPY trimer **36c** exhibited interesting recognition properties toward alkali metal ions. **36c** showed an absorbance band at 650 nm and exhibited near-IR fluorescence at 750 nm. The fluorescence quantum yield was $\Phi_{\text{em}} = 0.48$, which is a high value in this red-shifted region. Upon complexation with an alkali metal cation, **36c** became wrapped around it as the result of cooperative interaction with fluorine atoms. This folding resulted in the shift of absorbance and fluorescence to shorter wavelengths because of the reduced π -conjugation over the

oligomeric molecular framework. Among alkali metal cations, **36c** showed selectivity toward Cs^+ ($\log K_a=5.28$ in $\text{CHCl}_3/\text{CH}_3\text{OH}=10:1$), whose complexation resulted in the appearance of an absorption band at 510 nm and fluorescence at 708 nm ($\Phi_{\text{em}}=0.41$). Thus, **36c** serves as a Cs^+ -selective fluorescent sensor, for which there is a higher demand in nuclear waste treatment.³⁸

Figure 15. (a) The chemical structures of linear BODIPY oligomers **36a–36e**. (b) Change in photophysical properties of **36c** caused by folding in response to Cs^+ cation.

4. Conclusion

BODIPY and its derivatives are among the most famous and frequently used dipyrroin complexes because of their outstanding photophysical properties. In this account, however, we first demonstrated that the N_2O_2 -type dipyrroin is an excellent ligand for the synthesis of diverse dipyrroin complexes that would be unstable or hard to prepare using a usual bidentate dipyrroin. These new dipyrroin complexes thus obtained should open a way to novel types of red/NIR-emissive fluorophores, electrogenerated chemiluminescent compounds, catalysts, molecular photo-devices, color filters, etc.

In addition, we here demonstrated the usefulness and potential of dipyrroin complexes in supramolecular chemistry. The one-, two- and three-dimensional supramolecular architectures are available because multidentate dipyrroin derivatives can be easily obtained through chemical modifications of the dipyrroin skeleton. We also described the binding ability of the fluorine atoms in BODIPY to cationic guests. This electrostatic interaction is sufficiently effective to capture the guest and to regulate a flexible host structure to create a functional response to an external stimulus.

Chemistry of dipyrroins is still quite limited though many studies have been reported. We thus believe that dipyrroin com-

plexes with a variety of main-group and transition elements will make a significant contribution to create new aspects of organic chemistry, photochemistry, supramolecular chemistry, materials science and molecular biology.

References

- (a) Wood, T. E.; Thompson, A. *Chem. Rev.* **2007**, *107*, 1831. (b) Baudron, S. A. *Dalton Trans.* **2013**, *42*, 7498.
- (a) Loudet, A.; Burgess, K. *Chem. Rev.* **2007**, *107*, 4891. (b) Ulrich, G.; Ziessel, R.; Harriman, A. *Angew. Chem. Int. Ed.* **2008**, *47*, 1184.
- (a) Tahtaoui, C.; Thomas, C.; Rohmer, F.; Klotz, P.; Duportail, G.; Mély, Y.; Bonnet, D.; Hibert, M. *J. Org. Chem.* **2007**, *72*, 269. (b) Ikeda, C.; Nabeshima, T. *Chem. Commun.* **2008**, 721. (c) Maeda, H.; Nishimura, Y.; Hiroto, S.; Shinokubo, H. *Dalton Trans.* **2013**, *42*, 15885. (d) Umeda, N.; Takahashi, H.; Kamiya, M.; Ueno, T.; Komatsu, T.; Terai, T.; Hanaoka, K.; Nagano, T.; Urano, Y. *ACS Chem. Biol.* **2014**, *9*, 2242.
- Kim, H.; Burghart, A.; Welch, M. B.; Reibenspies, J.; Burgess, K. *Chem. Commun.* **1999**, 1889.
- (a) Tomimori, Y.; Okujima, T.; Yano, T.; Mori, S.; Ono, N.; Yamada, H.; Uno, H. *Tetrahedron* **2011**, *67*, 3187. (b) Okujima, T.; Shida, Y.; Ohara, K.; Tomimori, Y.; Nishioka, M.; Mori, S.; Nakae, T.; Uno, H. *J. Porphyrins Phthalocyanines* **2014**, *18*, 752.
- (a) Kubo, Y.; Minowa, Y.; Shoda, T.; Takeshita, K. *Tetrahedron Lett.* **2010**, *51*, 1600. (b) Kubo, Y.; Watanabe, K.; Nishiyabu, R.; Hata, R.; Murakami, A.; Shoda, T.; Ota, H. *Org. Lett.* **2011**, *13*, 4574.
- Ikeda, C.; Ueda, S.; Nabeshima, T. *Chem. Commun.* **2009**, 2544.
- Sakamoto, N.; Ikeda, C.; Yamamura, M.; Nabeshima, T. *J. Am. Chem. Soc.* **2011**, *133*, 4726.
- (a) Li, F.; Yang, S. I.; Ciringh, Y.; Seth, J.; Martin, III, C. H.; Singh, D. L.; Kim, D.; Birge, R. R.; Bocian, D. F.; Holten, D.; Lindsey, J. S. *J. Am. Chem. Soc.* **1998**, *120*, 10001. (b) Sazanovich, I. V.; Kirmaier, C.; Hindin, E.; Yu, L.; Bocian, D. F.; Lindsey, J. S.; Holten, D. *J. Am. Chem. Soc.* **2004**, *126*, 2664. (c) Kee, H. L.; Kirmaier, C.; Yu, L.; Thamyongkit, P.; Youngblood, W. J.; Calder, M. E.; Ramos, L.; Noll, B. C.; Bocian, D. F.; Scheidt, W. R.; Birge, R. R.; Lindsey, J. S.; Holten, D. *J. Phys. Chem. B* **2005**, *109*, 20433.
- Yamamura, M.; Albrecht, M.; Albrecht, M.; Nishimura, Y.; Arai, T.; Nabeshima, T. *Inorg. Chem.* **2014**, *53*, 1355.
- (a) Chuit, C.; Corriu, R. J. P.; Reye, C.; Young, J. C. *Chem. Rev.* **1993**, *93*, 1371. (b) Tacke, R.; Burschka, C.; Richter, I.; Wagner, B.; Willeke, R. *J. Am. Chem. Soc.* **2000**, *122*, 8480.
- Yamamura, M.; Takizawa, H.; Sakamoto, N.; Nabeshima, T. *Tetrahedron Lett.* **2013**, *54*, 7049.
- (a) Nakano, K.; Kobayashi, K.; Nozaki, K. *J. Am. Chem. Soc.* **2011**, *133*, 10720. (b) Ohkawara, T.; Suzuki, K.; Nakano, K.; Mori, S.; Nozaki, K. *J. Am. Chem. Soc.* **2014**, *136*, 10728.
- Ikeda, C.; Maruyama, T.; Nabeshima, T. *Tetrahedron Lett.* **2009**, *50*, 3349.
- Goze, C.; Ulrich, G.; Mallon, L. J.; Allen, B. D.; Harriman, A.; Ziessel, R. *J. Am. Chem. Soc.* **2006**, *128*, 10231.
- Unpublished result.
- Yamamura, M.; Yazaki, S.; Seki, M.; Matsui, Y.; Ikeda, H.; Nabeshima, T. *Org. Biomol. Chem.* **2015**, *13*, 2574.
- Settsune, J.; Omae, S. *Chem. Lett.* **2012**, *41*, 168.
- (a) Rausaria, S.; Kamadulski, A.; Rath, N. P.; Bryant, L.; Chen, Z.; Salvemini, D.; Neumann, W. L. *J. Am. Chem. Soc.* **2011**, *133*, 4200. (b) Ghachtouli, S. E.; Wójcik, K.; Copey, L.; Szydlowski, F.; Framery, E.; Goux-Henry, C.; Billon, L.; Charlot, M.-F.; Guillot, R.; Andrioletti, B.; Aukauloo, A. *Dalton Trans.* **2011**, *40*, 9090.
- Feng, Y.; Burns, L. A.; Lee, L.-C.; Sherrill, C. D.; Jones, C. W.; Murdock, C. *Inorg. Chim. Acta* **2015**, *430*, 30.
- Kochem, A.; Chiang, L.; Baptiste, B.; Philouze, C.; Leconte, N.; Jarjays, O.; Storr, T.; Thomas, F. *Chem. Eur. J.* **2012**, *18*, 14590.
- (a) Halper, S. R.; Malachowski, M. R.; Delaney, H. M.; Cohen, S. M. *Inorg. Chem.* **2004**, *43*, 1242. (b) Halper, S. R.; Cohen, S. M. *Inorg. Chem.* **2005**, *44*, 4139. (c) Heinze, K.; Reinhart, A. *Inorg. Chem.* **2006**, *45*, 2695. (d) Salazar-Mendoza, D.; Baudron, S. A.; Hosseini, M. W. *Inorg. Chem.* **2008**, *47*, 766. (e) Matsuoka, R.; Toyoda, R.; Sakamoto, R.; Tsuchiya, M.; Hoshiko, K.; Nagayama, T.; Nonoguchi, Y.; Sugimoto, K.; Nishibori, E.; Kawai, T.; Nishihara, H. *Chem. Sci.* **2015**, *6*, 2853.
- (a) Yaghi, O. M.; Li, H.; Davis, C.; Richardson, D.; Groy, T. L. *Acc. Chem. Res.* **1998**, *31*, 474. (b) Eddaoudi, M.; Moler, D. B.; Li, H.; Chen, B.; Reineke, T. M.; O'Keeffe, M.; Yaghi, O. M. *Acc. Chem. Res.* **2001**, *34*, 319. (c) Moulton, B.; Zaworotko, M. J. *Chem. Rev.* **2001**,

- 24) Pogozhev, D.; Baudron, S. A.; Hosseini, M. W. *Inorg. Chem.* **2010**, *49*, 331.
- 25) (a) Halper, S. R.; Cohen, S. M. *Angew. Chem. Int. Ed.* **2004**, *43*, 2385. (b) Ma, L.; Patrick, B. O.; Dolphin, D. *Chem. Commun.* **2011**, *47*, 704. (c) Béziau, A.; Baudron, A.; Guenet, A.; Hosseini, M. W. *Chem. Eur. J.* **2013**, *19*, 3215.
- 26) (a) Geim, A. K.; Novoselov, A. S. *Nat. Mater.* **2007**, *6*, 183. (b) Bonaccorso, F.; Sun, Z.; Hasan, T.; Ferrari, A. C. *Nat. Photonics* **2010**, *4*, 611.
- 27) Sakamoto, R.; Hoshiko, K.; Liu, Q.; Yagi, T.; Nagayama, T.; Kusaka, S.; Tsuchiya, M.; Kitagawa, Y.; Wong, W.-Y.; Nishihara, H. *Nat. Commun.* **2015**, *6*, 6713.
- 28) (a) Batten, S. R.; Robson, R. *Angew. Chem. Int. Ed.* **1998**, *37*, 1460. (b) Kitagawa S.; Kitaura, R.; Noro, S. *Angew. Chem. Int. Ed.* **2004**, *43*, 2334. (c) Murray, L. J.; Dinca, M.; Long, J. R. *Chem. Soc. Rev.* **2009**, *38*, 1294. (d) Chen, B.; Xiang, S.; Qian, G. *Acc. Chem. Res.* **2010**, *43*, 1115.
- 29) (a) Stork, J. R.; Thoi, V. S.; Cohen, S. M. *Inorg. Chem.* **2007**, *46*, 11213. (b) Halper, S. R.; Do, L.; Stork, J. R.; Cohen, S. M. *J. Am. Chem. Soc.* **2006**, *128*, 15255. (c) Béziau, A.; Baudron, S. M.; Fluck, A.; Hosseini, M. W. *Inorg. Chem.* **2013**, *52*, 14439.
- 30) Lee, C. Y.; Farha, O. K.; Hong, B. J.; Sarjeant, A. A.; Nguyen, S. T.; Hupp, J. T. *J. Am. Chem. Soc.* **2011**, *133*, 15858.
- 31) Richards, G. J.; Gobo, Y.; Yamamura, M.; Nabeshima, T. *New J. Chem.* **2015**, *39*, 5886.
- 32) Allred, A. L. *J. Inorg. Nucl. Chem.* **1961**, *17*, 215.
- 33) (a) Plenio, H. *Chem. Rev.* **1997**, *97*, 3363. (b) Plenio, H. *ChemBioChem* **2004**, *5*, 650. (c) Takemura, H.; Kon, N.; Yasutake, M.; Kariyazono, H.; Shinmyozu, T.; Inazu, T. *Angew. Chem. Int. Ed.* **1999**, *38*, 959. (d) Takemura, H.; Kariyazono, H.; Yasutake, M.; Kon, N.; Tani, K.; Sako, K.; Shinmyozu, T.; Inazu, T. *Eur. J. Org. Chem.* **2000**, 141. (e) Takemura, H.; Kon, N.; Kotoku, M.; Nakashima, S.; Otsuka, K.; Yasutake, M.; Shinmyozu, T.; Inazu, T. *J. Org. Chem.* **2001**, *66*, 2778. (f) Chi, K.-W.; Shim, K. T.; Huh, H.; Lee, U.; Park, Y. J. *Bull. Korean Chem. Soc.* **2005**, *26*, 393. (g) Sazonov, P. K.; Minacheva, L. Kh.; Churakov, A. V.; Sergienko, V. S.; Artamkina, G. A.; Oprunenko, Y. F.; Beletskaya, I. P. *Dalton Trans.* **2009**, 843.
- 34) Sakamoto, N.; Ikeda, C.; Nabeshima, T. *Chem. Commun.* **2010**, *46*, 6732.
- 35) Sakamoto, N.; Ikeda, C.; Yamamura, M.; Nabeshima, T. *Chem. Commun.* **2012**, *48*, 4818.
- 36) Weissleder, R.; Ntziacharistos, V. *Nat. Med.* **2003**, *9*, 234.
- 37) Grätzel, M. *J. Photochem. Photobiol., C* **2003**, *4*, 145.
- 38) (a) Hill, C.; Dozol, J.-F.; Lamare, V.; Rouquette, H.; Eymard, S.; Tournois, B.; Vicens, J.; Asfari, Z.; Bressot, C.; Ungaro, R.; Casnati, A. *J. Inclusion Phenom. Mol. Recognit. Chem.* **1994**, *19*, 399. (b) Nabeshima, T.; Yoshihira, Y.; Saiki, T.; Akine, S.; Horn, E. *J. Am. Chem. Soc.* **2003**, *125*, 28.

PROFILE

Tatsuya Nabeshima is a Professor at the University of Tsukuba. He received his B.S. in 1979 from The University of Tokyo, M.S. in 1981 from the University of Tsukuba, and Ph.D. in 1985 from Kyoto University. In 1985, he joined Stanford University as a postdoctoral fellow. He became Assistant Professor in 1987. He moved to Gunma University as an assistant professor in 1989 and was promoted to Associate Professor in 1991. He returned to the University of Tsukuba as an associate professor in 1995, and was promoted to Professor in 1999. In 2004 he was a Professor of the Graduate School of Pure and Applied Sciences, University of Tsukuba, and from 2010 to 2012 and in 2015 he is again Director of Tsukuba Research Center for Interdisciplinary Materials Science (TIMS), University of Tsukuba. His research interests cover artificial receptors, molecular recognition, artificial allosteric and responding molecular systems, and organic-inorganic supramolecular systems. He received The Chemical Society of Japan Award for Creative Work in 2008.

Masaki Yamamura received his Ph.D. from The University of Tokyo under Prof. Takayuki Kawashima (2007). He worked as a JSPS fellow at Gunma University under Prof. Masafumi Unno (2007–2008). He moved to University of Tsukuba as an Assistant Professor to work with Prof. Tatsuya Nabeshima (2008). He was promoted to a Lecturer at University of Tsukuba (2012). His current research interest is focused on supramolecular chemistry based on heteroatom chemistry.

Gary J. Richards is currently an Associate Professor of Chemistry at Ochanomizu University, Tokyo. He obtained his Ph.D. in Chemistry from the University of Hull, UK in 2001. He completed 2 years' Post-doctoral research in OLED materials at Oxford University in 2003 after which he moved to Japan to work in the Supermolecules group at NIMS in Japan researching nitrogen-rich pi-conjugated materials. He worked as an Assistant Professor under supervision of Professor T. Nabeshima at Tsukuba University researching novel mercury-sensing BODIPY derivatives. His main research interests include supramolecular chemistry and pi-conjugated materials.

Takashi Nakamura received his Ph.D. from the University of Tokyo under Prof. Mitsuhiro Shionoya (2013). In 2013, he joined the laboratory of Prof. Akira Harada at Osaka University as a postdoctoral fellow. He has worked as an assistant professor with Prof. Tatsuya Nabeshima at University of Tsukuba since 2014. His current research interest is the precise construction of supramolecular systems and exploration of their functions.