ChemPubSoc Europe

DOI: 10.1002/chem.201501464

CHEMISTRY A European Journal Full Paper

Dyes/Pigments

Benzo[*c*,*d*]indole-Containing Aza-BODIPY Dyes: Asymmetrization-Induced Solid-State Emission and Aggregation-Induced Emission Enhancement as New Properties of a Well-Known Chromophore

Soji Shimizu,*[a, b] Ai Murayama,[c] Takuya Haruyama,[c] Taku Iino,[c] Shigeki Mori,[d] Hiroyuki Furuta,[a, b] and Nagao Kobayashi*[c, e]

Abstract: A series of symmetric and asymmetric benzo[*c*,*d*]-indole-containing aza boron dipyrromethene (aza-BODIPY) compounds was synthesized by a titanium tetrachloride-mediated Schiff-base formation reaction of commercially available benzo[*c*,*d*]indole-2(1*H*)-one and heteroaromatic amines. These aza-BODIPY analogues show different electronic structures from those of regular aza-BODIPYs, with hypsochromic shifts of the main absorption compared to their BODIPY counterparts. In addition to the intense fluorescence in solution, asymmetric compounds exhibited solid-state fluorescence due to significant contribution of the vibronic bands to both absorption and fluorescence as well as reduced fluorescence quenching in the aggregates. Finally, aggregation-induced emission enhancement, which is rare in BODIPY chromophores, was achieved by introducing a nonconjugated moiety into the core structure.

Introduction

4,4-Difluoro-4-bora-3*a*,4*a*-diaza-*s*-indacene (BODIPY), a boron difluoride complex of dipyrrin,[1–4] is one of the most widely investigated functional chromophores and is frequently utilized in a variety of fields, such as bioimaging,[5] chemosensors,[6] laser dyes,[7] photodynamic therapy,[8] optoelectronic materials including light-emitting diodes[9] and photovoltaics,[10] and multichromophore systems for artificial photosynthetic models,[11] due to its intense absorption in the visible region and environmentally insensitive fluorescent properties. Aza-BODIPY,[12] in which a carbon atom at the pyrrole-bridging position in BODIPY denoted *meso* position is replaced with a nitrogen atom, is known to exhibit bathochromic shifts of the absorption and emission compared to the corresponding BODIPY. Because of the absorption and emission of regular aza-BODIPYs above 650 nm in the visible region, intensive research has recently focused on their potential applications, in particular in the field of bioimaging.[13] The bathochromic shift can be explained by the effective stabilization of the LUMO energy level by the higher electronegativity of nitrogen than carbon at the *meso* position, on which MO coefficients were found for the LUMO but not for the HOMO in DFT calculations.[14] In contrast to BODIPYs, the synthetic availability of aza-BODIPYs still remains limited, which hinders the derivatization or functionalization required for applications. Recently, we reported a facile synthesis of dimeric aza-BODIPY analogues from heteroaromatic amines and diketopyrrolopyrrole.[15] In this reaction, lactam moieties of the diketopyrrolopyrrole were successfully converted to an aza-BODIPY structure by a Schiff-base formation reaction in the presence of titanium tetrachloride and triethylamine. It was therefore inferred that these reaction conditions could be applied to other lactams to synthesize novel aza-BODIPY analogues. As a synthetic target for this method, benzo[*c*,*d*]indole-containing aza-BODIPY **1**[16] was selected because of its hypsochromic shift of the absorption spectrum compared to its *meso*-carbon counterpart **2** (Figure 1),[17] which is a rare exception to the above-mentioned general trend in the absorption and fluorescence spectra of BODIPYs and aza-BODIPYs. Although this compound was once reported, it was neither thoroughly investigated in the original papers nor substantially addressed in the previous literature. Moreover, optical properties other than absorption, such as fluorescence, have not yet been elucidated. Herein, we report the synthesis of a series of benzo[*c*,*d*]indole-containing aza-

[a] *Prof. Dr. S. Shimizu, Prof. Dr. H. Furuta*
Department of Chemistry and Biochemistry
Graduate School of Engineering
Kyushu University, Fukuoka 819-0395 (Japan)
E-mail: ssoji@cstf.kyushu-u.ac.jp

[b] *Prof. Dr. S. Shimizu, Prof. Dr. H. Furuta*
Center for Molecular Systems (CMS)
Kyushu University, Fukuoka 819-0395 (Japan)
E-mail: ssoji@cstf.kyushu-u.ac.jp

[c] *A. Murayama, T. Haruyama, T. Iino, Prof. Dr. N. Kobayashi*
Department of Chemistry, Graduate School of Science
Tohoku University, Sendai 980-8578 (Japan)
E-mail: nagaok@m.tohoku.ac.jp

[d] *Dr. S. Mori*
Division of Material Science, Advanced Research Support Center
Ehime University, Matsuyama 790-8577 (Japan)

[e] *Prof. Dr. N. Kobayashi*
Faculty of Textile Science and Technology, Shinshu University
Ueda 386-8567 (Japan)

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.201501464.

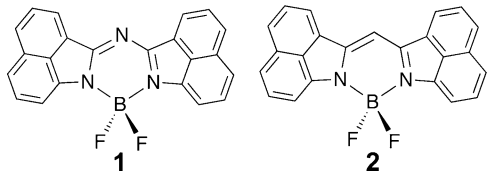


Figure 1. Structures of benzo[*c*,*d*]indole-containing aza-BODIPY **1** and its *meso*-carbon counterpart **2**.

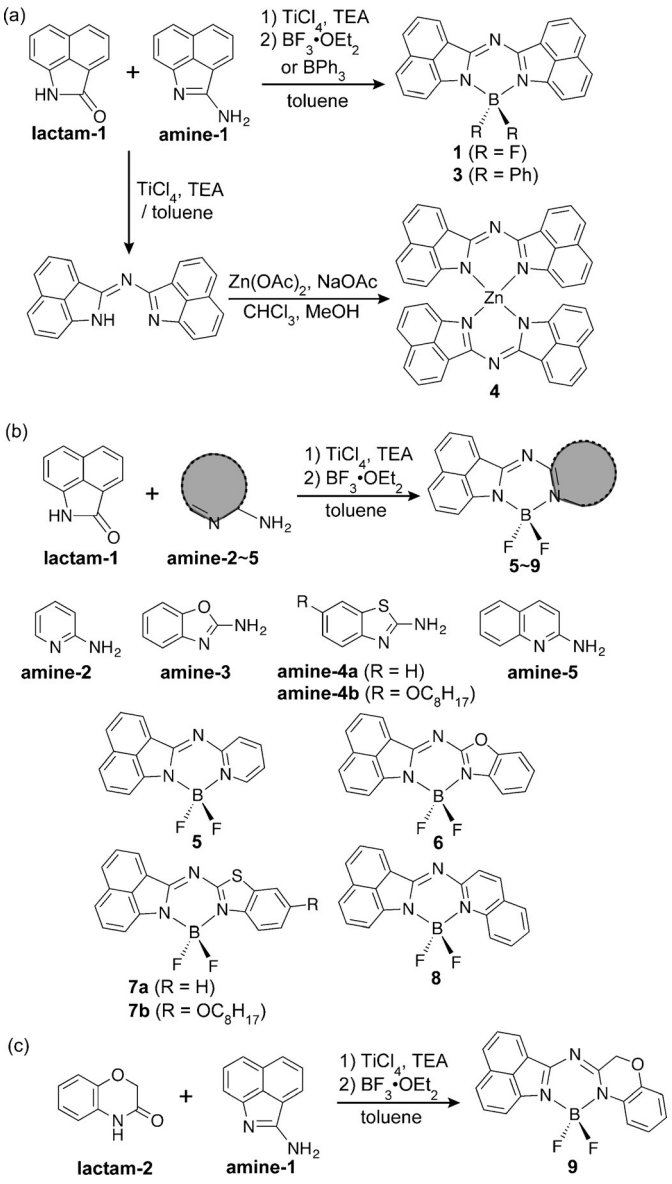
BODIPYs using our synthetic method.[18] In addition to addressing the hypsochromic shift of **1** from **2**, novel aspects of the aza-BODIPY chromophore, such as enhanced solid-state emission by asymmetrization of the structure and aggregation-induced enhancement of emission by incorporating a nonconjugated moiety into the core structure, were achieved.

Results and Discussion

Synthesis and crystal structures of benzo[*c*,*d*]indole-containing aza-BODIPYs

Benzo[*c*,*d*]indole-containing aza-BODIPY **1** was synthesized in 41% yield by a Schiff-base formation reaction of commercially available benzo[*c*,*d*]indole-2(1*H*)-one (**lactam-1**) and benzo[*c*,*d*]indole-2-amine (**amine-1**), which was derived in four steps from **lactam-1**,[16,19] in the presence of $TiCl_4$ and triethylamine (TEA)[20] followed by in situ coordination of boron difluoride by addition of BF_3•OEt_2 to the reaction mixture (Scheme 1 a).[15] The substituents on the boron atom can be changed from fluoride to phenyl by using triphenylborane instead of BF_3•OEt_2 (**3** in Scheme 1 a). A dipyrrin ligand structure of **1**, which can also be synthesized without addition of boron reagent in the last step, facilely formed zinc complex **4**. In addition to these symmetric aza-BODIPYs, asymmetric types **5**–**9** were also synthesized (Scheme 1 b and c) from **lactam-1** and heteroaromatic amines (**amine-2**–**5**) or from **amine-1** and 2*H*-1,4-benzoxazine-3(4*H*)-one (**lactam-2**). Compounds **5** and **7 a** can also be synthesized from the opposite combination of an amine and lactams, namely, **amine-1** with 2(3*H*)-benzothiazolone and 2(3*H*)-benzoxazolone, but the yields were lower than those of the reactions of **lactam-1** with **amine-2** and **amine-4 a**.

All of these aza-BODIPYs were characterized by high-resolution MALDI-TOF Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometry and ^{1}H NMR spectroscopy (see the Supporting Information). All of the structures, except those of **1** and **4**, were further unambiguously elucidated by X-ray crystallography (Figure 2 and Figure S1 in the Supporting Information). In the molecular packing diagram, both H- and J-type arrangements or intermediate arrangements were observed for the nearest neighbors with interplanar separations of the mean planes of molecules ranging from 3.3 to 3.7 Å, apart from **7 b**, **8**, and **9**, in which only J-type packing was found (Figure 3 and Figure S1 in the Supporting Information). In addition, due to its slightly deformed structure, **9** is not arranged in a parallel manner, but in a rather zigzag manner.



Scheme 1. Synthesis of symmetric (a) and asymmetric (b, c) benzo[*c*,*d*]indole-containing aza-BODIPY analogues.

Optical properties

The absorption spectra of the aza-BODIPYs in the visible region were characterized by either two intense bands or a broad band with a lower-energy shoulder (Figure 4 a and Table 1). Compared with the main absorption of asymmetric compounds **5**–**9** at 400–500 nm, symmetric compounds **1**, **3**, and **4** exhibited bathochromic shifts due to the larger conjugated system of the benzo[*c*,*d*]indole moiety than those of the other heteroaromatic moieties in **5**–**9**. Among the symmetric compounds, **3** and **4** exhibited a further bathochromic shift relative to **1**. On the basis of time-dependent (TD) DFT calculations at the B3LYP/6-31G(d) level (Table S1 and Figure S2 in the Supporting Information), which assigned these main absorptions as a HOMO–LUMO transition, the observed higher-energy absorption, such as the band of **1** at 503 nm, can be ascribed

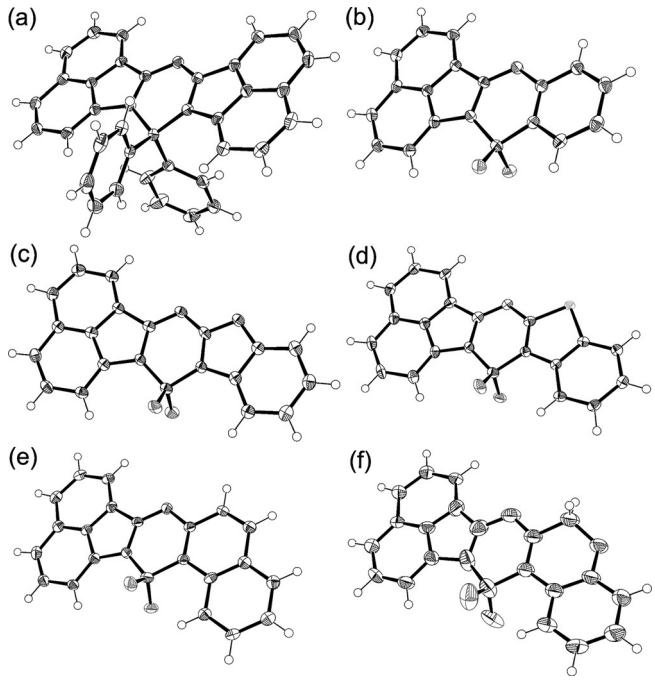


Figure 2. Crystal structures of a) **3**, b) **5**, c) **6**, d) **7a**, e) **8**, and f) **9**. The thermal ellipsoids were scaled to the 50% probability level.

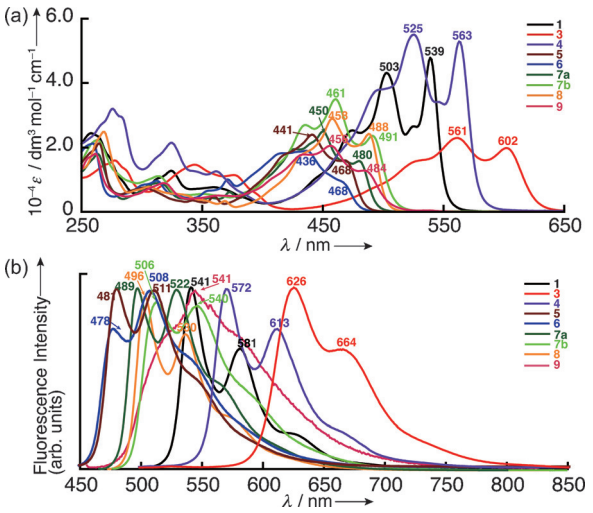


Figure 4. a) UV/Vis absorption and b) fluorescence spectra of benzo[*c*,*d*]indole-containing aza-BODIPY analogues in $CHCl_3$.

to the vibronic 0–1 band. In the case of the asymmetric compounds, this vibronic 0–1 band is more intense, and is observed as a broad, main band, so that the 0–0 band can be detected as a less-intense lower-energy band or a kind of shoulder absorption. This significant contribution of the vibronic bands infers a structural change of these rigid chromophores in the excited state.

The DFT and TDDFT calculations also gave an explanation of the reported hypsochromic shift of **1** (λ_{max} = 539 nm) versus **2** (λ_{max} = 622 nm).[16,17] Large MO coefficients of the HOMO were found on the *meso* position, whereas a node was found at the *meso* position in the LUMO (Figure S3 in the Supporting Information). Therefore, replacement of a carbon atom at the *meso* position of **2** with a more electronegative nitrogen atom causes stabilization of the HOMO, which results in the observed hypsochromic shift of **1** due to the increase of the HOMO–LUMO gap (Table S1 in the Supporting Information).

All of the benzo[*c*,*d*]indole-containing aza-BODIPYs exhibited intense fluorescence with Stokes shifts ranging from 69 to 1244 cm^{-1} and intense vibronic 0–1 bands (Figure 4b and Table 1). Despite the small Stokes shifts, except for **9**, overlap of the absorption and fluorescence spectra is considerably reduced for the asymmetric compounds due to the contribution of the vibronic bands to the absorption and emission (Figure 5 and Figure S4 in the Supporting Information). The absolute fluorescence quantum yields Φ_F were high and ranged from 0.83 to 0.60, except for **3**, **4**, **7b**, and **9**, among which the fluo-

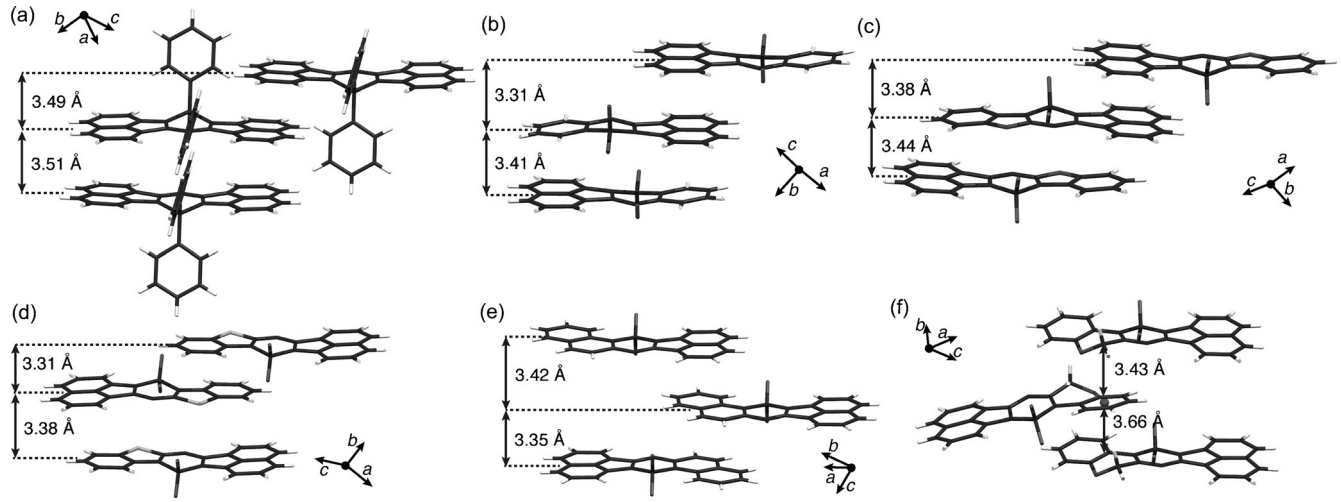


Figure 3. Molecular packing diagrams of a) **3**, b) **5**, c) **6**, d) **7a**, e) **8**, and f) **9**. Interplanar distances between the mean planes of molecules excluding the two fluorine atoms are shown in a)–e). Distances of the mean planes of over- and underlying molecules excluding the two fluorine atoms from the center of the benzene ring of the benzoxazine moiety, represented by a gray dot, are shown in f).

Table 1. Summary of optical properties of aza-BODIPY analogues in $CHCl_3$ and in the solid state.

Compound	λ_{00}^{abs} [nm]	lg ε_{00}	λ_{00}^{em} [nm]	Stokes shift [cm^{-1}]	Φ_{CHCl_3} [a]	Φ_{PMMA} [b]	Φ_{sol} [c]	τ_F [ns]	k_r [$10^8\ s^{-1}$] [d]	k_{nr} [$10^8\ s^{-1}$] [e]
1	539	4.68	541	69	0.60	0.30	0.08	5.0	1.2	0.8
3	602	4.30	626	637	0.13	0.15	0.04	6.5	0.2	1.3
4	563	4.72	572	279	0.26	0.15	0.02	2.3	1.1	3.2
5	468	4.20	481	534	0.83	0.82	0.20	7.0	1.2	0.2
6	468 [f]	3.94	478	447	0.70	0.71	0.24	5.9	1.2	0.5
7a	480	4.20	489	383	0.81	0.81	0.27	6.0	1.4	0.3
7b	491	4.38	506	603	0.38	0.43	0.22	2.5	1.5	2.5
8	488	4.38	496	331	0.84	0.82	0.13	5.8	1.4	0.3
9	484	4.11	515 [f]	1244	0.05	0.13	0.14	0.30	1.7	32

[a] Absolute fluorescence quantum yield in $CHCl_3$. [b] Absolute fluorescence quantum yield in PMMA film. [c] Absolute fluorescence quantum yield of amorphous drop-cast film. [d] Rate constant for radiative decay in $CHCl_3$: $k_r = \Phi_F/\tau_F$. [e] Rate constant for nonradiative decay in $CHCl_3$: $k_{nr} = (1-\Phi_F)/\tau_F$. [f] Shoulder bands were assigned as a 0–0 band.

rescence of **9** was nearly quenched ($\Phi_F = 0.05$). Structurally flexible moieties of these less-fluorescent compounds, such as phenyl groups on the boron atom, long alkoxyl chains, and a nonconjugated moiety, may enhance nonradiative decay processes, which can be evidenced by short fluorescence lifetimes and large nonradiative rate constants.

In the solid state, the benzo[*c*,*d*]indole-containing aza-BODIPYs showed three types of emission behaviors, reflecting their structural features (Figure 5, Table 1, and Figure S4 in the Supporting Information). The emission of symmetric compounds **1**, **3**, and **4** was nearly quenched in the solid state of a drop-cast film, which exhibited Φ_F values of 0.02–0.08 (Figure S5 in the Supporting Information). Aggregation-caused quenching (ACQ) is a normal behavior for fluorophores with small Stokes shifts. In contrast, in the case of the asymmetric compounds with a fully conjugated structure (**5**–**8**), moderately intense emission with $\Phi_F = 0.13$–0.27 was observed, despite the small Stokes shifts. In general, solid-state fluorescent compounds including BODIPYs either exhibit large Stokes shifts in solution[21,22] or have bulky substituents[23] that minimize interchromophore interactions in the solid state. Neither is the case for asymmetric compounds **5**–**8**. Instead, the solid-state fluorescence in this case can be explained in terms of the contribution of the vibronic bands to both the absorption and emission, as described above, and the molecular packing in the solid state. The small overlap of the absorption and emission caused by intensification of the 0–1 band reduces self-absorption in the solid state. The fluorescence spectra of the poly(methyl methacrylate) (PMMA) films, which exhibited similar absorption spectra to those in solution, showed decrease or disappearance of the 0–0 emission band due to self-absorption. The larger spectral overlaps of symmetric compounds **1**, **3**, and **4** compared to the asymmetric species results in significant quenching of the emission with a decrease of Φ_F, whereas Φ_F of the asymmetric compounds is almost entirely retained (Figure 5, Table 1, and Figures S4 and S6 in the Supporting Information). The amorphous films prepared by a drop-casting method exhibited broadening and a bathochromic shift of the emission. The emission of the symmetric compounds was further significantly

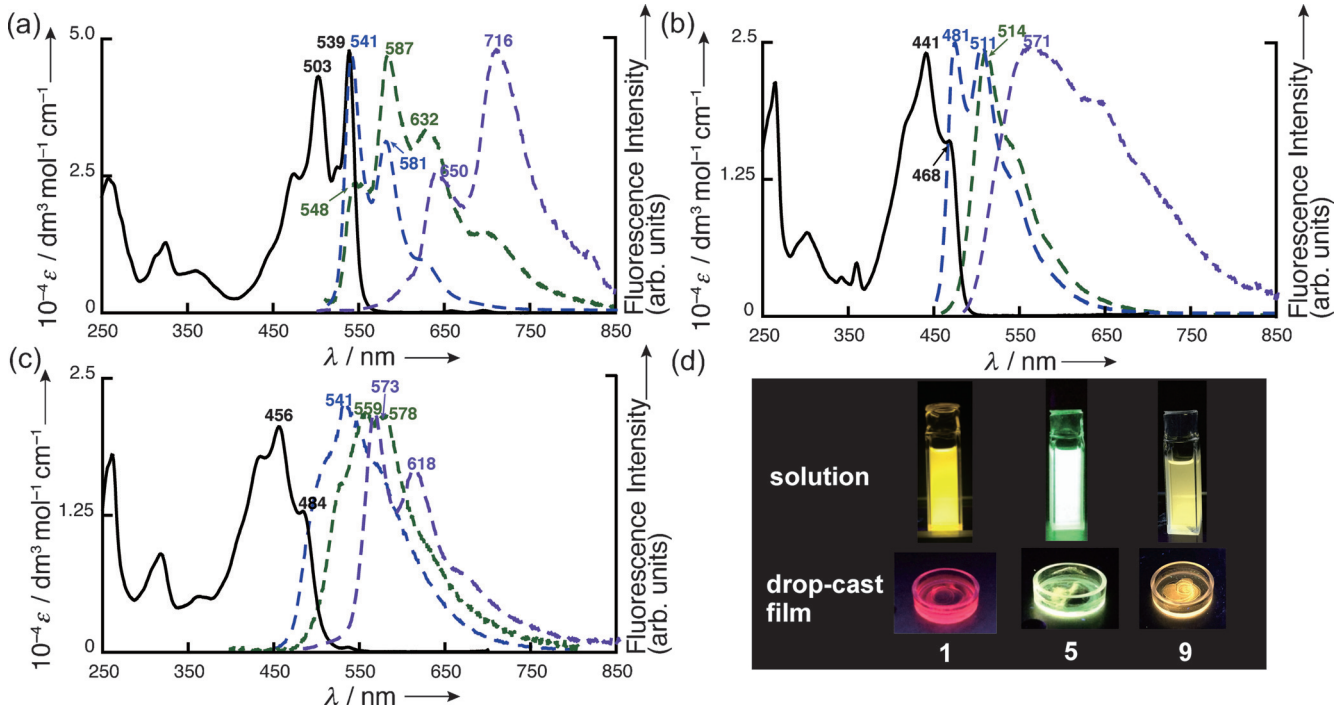


Figure 5. UV/Vis absorption in $CHCl_3$ (black solid line) and fluorescence spectra of a) **1**, b) **5**, and c) **9** in $CHCl_3$ solution (blue dashed line), a PMMA film (green dashed line), and a drop-cast film (violet dashed line). d) Photographs of solutions (top) and drop-cast films (bottom) under irradiation by 365 nm light.

quenched, whereas that of the asymmetric compounds was rather moderately quenched (Figure 5, Table 1, and Figures S4 and S6 in the Supporting Information). Despite ACQ, the asymmetric compounds were still fluorescent, which can be explained by the manner of aggregation of these compounds in the amorphous films. Considering that H-type and J-type arrangements or intermediate arrangements were present in the molecular packing diagrams, both H- and J-type dimer formation can be expected for aggregates in the amorphous films. According to the Kasha exciton theory,[24] H-type aggregates are nonfluorescent because the lowest excited state becomes forbidden.[25] As a rare exception, Würthner et al. reported emission from H-type aggregates of merocyanine dyes and concluded that small deviations of the direction of the transition dipole moments between nearest neighbors may reduce the forbidden nature.[26] A similar mechanism may be possible in the current case. Due to the asymmetric structures, the transition dipole moments would not be cancelled out, even if molecules form H-type aggregates, so that the emission is not completely quenched.

In a stark contrast to the almost complete and partial ACQ behaviors of the symmetric (**1**, **3**, and **4**) and asymmetric (**5**–**8**) aza-BODIPYs, respectively, the emission of **9**, which has a nonconjugated moiety in the core structure, was enhanced on going from solution to a PMMA film and an amorphous film with an increase in Φ_F from 0.05 to 0.14 (Figure 5, Table 1, and Figures S4 and S6 in the Supporting Information). This behavior can be recognized as a kind of aggregation-induced emission enhancement (AIEE).[27] To confirm the AIEE behavior of **9**, changes in the fluorescence spectra and development of Φ_F were investigated on increasing the water fraction in a THF solution of **9** (Figure 6). The fluorescence spectra, which are similar to that observed for the amorphous film, gradually developed at high water fraction, while Φ_F increased from 0.02 at 0% to 0.23 at 96% water fraction. These results clearly indicate that aggregation in the solid state reduces the molecular dynamics caused by the nonconjugated sp^3 carbon moiety. To the best of our knowledge, **9** is the first aza-BODIPY system exhibiting AIEE behavior.

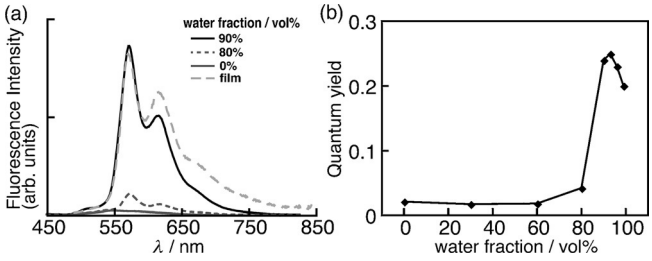


Figure 6. a) Changes of fluorescence spectra of **9** depending on water fraction of THF/water mixtures. The fluorescence spectrum of a drop-cast film of **9** is shown as a reference (gray dashed line). b) Dependence of the quantum yield of **9** on water fraction.

Conclusion

The titanium tetrachloride-mediated Schiff-base formation reaction of lactam compounds was applied to benzo[*c*,*d*]indole-2(1*H*)-one with the initial aim of elucidating the optical properties of benzo[*c*,*d*]indole-containing aza-BODIPY **1**, but resulted in an encounter with rather unexpected aspects of the properties of aza-BODIPY chromophores. The hypsochromic shifts of these aza-BODIPYs, which were caused by their different electronic structures compared to regular aza-BODIPYs, imply that there is a room for tuning the absorption and emission properties of aza-BODIPYs by incorporating heteroaromatic moieties in place of pyrrole or isoindole rings. The significant contribution of the vibronic bands to both absorption and emission is a novel strategy towards solid-state emission. Finally the incorporation of a nonconjugated moiety in the core structure of the chromophores enables AIEE responses. With this knowledge as a base, novel chromophore systems applicable in a variety of fields can be developed.

Experimental Section

General procedures

Electronic absorption spectra were recorded on a JASCO V-570 spectrophotometer. Fluorescence spectra of $CHCl_3$ solutions and drop-cast films were measured on a Hitachi F-4500 spectrofluorimeter and on a Horiba Fluorolog-3 spectrofluorimeter, respectively. Absolute fluorescence quantum yields and fluorescence spectra of PMMA films were measured on a Hamamatsu Photonics C9920-03G calibrated integrating-sphere system. The fluorescence lifetime was measured with a picosecond light pulser (Hamamatsu Photonics C4725: 408 nm, 59 ps FWHM) and a streak scope (Hamamatsu Photonics C4334-02). ^1H NMR spectra were recorded on a Bruker AVANCE III 500 spectrometer (operating at 500.133 MHz for ^1H) by using residual proton signals of solvents as internal references for ^1H ($\delta = 7.26$ ppm for $CDCl_3$, $\delta = 5.32$ ppm for CD_2Cl_2, and $\delta = 2.50$ ppm for [D_6]DMSO). High-resolution mass spectra were recorded on a Bruker Daltonics solariX 9.4T spectrometer. Preparative separations were performed by column chromatography on silica gel (Wako). Toluene that was used for the synthesis of benzo[*c*,*d*]indole-containing aza-BODIPYs was distilled over CaH_2 prior to use. All other reagents and solvents were of commercial reagent grade and were used without further purification, except where noted.

Crystallographic data collection and structure refinement

Suitable crystals of **3**, **5**, **6**, **7a**, **7b**, **8**, and **9** for X-ray analysis were obtained by slow diffusion of methanol or hexane into $CHCl_3$ solutions. Data were collected on a Bruker APEXII CCD diffractometer with $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å) at $-173(2)^\circ C$ and on a Rigaku R-AXIS RAPID diffractometer with $Cu_{K\alpha}$ radiation ($\lambda = 1.54187$ Å). The structures were solved by a direct method (SHLEXS-97[28] and Sir 2011[29]) and refined by using a full-matrix least-squares technique [SHELXL64 (SHELXL-2013)].[28] Yadokari-XG[30] software was used as a GUI for SHELXL-2013. CCDC 1050935 (**3**), 1050936 (**5**), 1050937 (**6**), 1050938 (**7a**), 1050939 (**7b**), 1050940 (**8**) and 1050941 (**9**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Computational methods

The Gaussian 09[31] software package was used to carry out DFT and TDDFT calculations with the B3LYP functional and 6-31G(d) basis set. Structural optimization was performed on model structures.

Sample preparation for solid-state fluorescence measurements

PMMA films for fluorescence measurements were prepared from a chloroform solution of PMMA (100 mg mL^{-1}) containing 0.2 wt% sample by using a drop-casting method. Amorphous film samples for fluorescence measurements were prepared by drop casting.

Synthesis of benzo[*c*,*d*]indole-containing aza-BODIPYs

Synthesis of 1: Benzo[*c*,*d*]indole-2-amine hydroiodide (**amine-1**, 100 mg, 0.34 mmol) and benzo[*c*,*d*]indole-2(1*H*)-one (**lactam-1**, 60 mg, 0.34 mmol) were dissolved in toluene (2 mL), and then TEA (1 mL) and $TiCl_4$ (0.05 mL) were added to the solution under reflux. After stirring for 15 min, $BF_3{\cdot}OEt_2$ (0.75 mL) was added, and the resulting mixture was further heated to reflux for 2 h. The reaction mixture was filtered, and the filtrate was added to water. The organic phase was extracted with chloroform and dried over Na_2SO_4. Finally, the product was purified by silica-gel column chromatography with chloroform as eluent and recrystallized from chloroform and methanol to afford **1** as an orange powder in 41% yield (51 mg, 0.14 mmol). HR-MALDI-FT-ICR-MS: *m/z* 368.1165 (calcd for $C_{22}H_{13}BF_2N_3$: 368.1165 [M^++H]); ^{1}H NMR (CD_2Cl_2, 500 MHz, 298 K): δ = 8.53 (d, J = 7.0 Hz, 2H), 8.28 (d, J = 7.5 Hz, 2H), 7.90 (m, 4H), 7.84 (d, J = 7.0 Hz, 2H), 7.73 ppm (dd, J_1 = 7.5, J_2 = 7.0 Hz, 2H); UV/Vis ($CHCl_3$): λ_{max} [nm] (ε [mol^{-1} dm^3 cm^{-1}]) = 539 (48000), 503 (43000).

Synthesis of 3: Benzo[*c*,*d*]indole-2-amine hydroiodide (**amine-1**, 0.51 g, 1.7 mmol) and benzo[*c*,*d*]indole-2(1*H*)-one (**lactam-1**, 0.30 g, 1.8 mmol) were dissolved in toluene (9 mL), and then TEA (5 mL) and $TiCl_4$ (0.25 mL) were added to the solution under reflux. After stirring for 30 min, triphenylborane (0.41 g, 1.7 mmol) was added, and the resulting mixture was further heated to reflux for 1.5 h. The reaction mixture was filtered, and the filtrate was added to water. The organic phase was extracted with chloroform and dried over Na_2SO_4. Finally the product was purified by silica gel column chromatography with chloroform as eluent and recrystallized from chloroform and methanol to afford **3** as an orange powder in 5.1% yield (42 mg, 0.086 mmol). HR-MALDI-FT-ICR-MS: *m/z* 484.1980 (calcd for $C_{34}H_{23}BN_3$: 484.1980 [M^++H]); ^{1}H NMR ($CDCl_3$, 500 MHz, 298 K): δ = 8.49 (d, J = 7.0 Hz, 2H), 8.13 (d, J = 8.0 Hz, 2H), 7.83 (dd, J_1 = 8.0, J_2 = 7.0 Hz 2H), 7.63 (m, 6H), 7.32 (m, 4H), 7.21 (m, 4H), 6.85 (d, J = 7.5 Hz, 2H); UV/Vis ($CHCl_3$): λ_{max} [nm] (ε [mol^{-1} dm^3 cm^{-1}]) = 602 (20000), 561 (23000).

Synthesis of 4: Benzo[*c*,*d*]indole-2-amine (**amine-1**, 0.20 g, 1.2 mmol) and benzo[*c*,*d*]indole-2(1*H*)-one (**lactam-1**, 0.12 g, 0.68 mmol) were dissolved in toluene (4 mL), and then TEA (2 mL) and $TiCl_4$ (0.1 mL) were added to the solution under reflux. After stirring for 2.5 h, the reaction mixture was filtered, and the filtrate was added to water. The organic phase was extracted with chloroform and dried over Na_2SO_4. After removal of solvent, the residue was dissolved in $CHCl_3$/MeOH (50 mL, 2/1). $Zn(OAc)_2$ (1.3 g, 6.8 mmol) and NaOAc (56 mg, 6.8 mmol) were then added, and the resulting mixture was heated to reflux overnight. The reaction mixture was washed with water, and the organic layer was extracted with chloroform. The extract was purified by silica-gel column chromatography with $CHCl_3$/MeOH as eluent and GPC-HPLC. Finally recrystallization from chloroform and hexane provided **4** as a red powder in 8.6% yield (41 mg, 0.058 mmol). HR-MALDI-FT-ICR-MS: *m/z* 701.1428 (calcd for $C_{44}H_{25}N_6Zn$: 701.1427 [M^++H]); ^{1}H NMR ($CDCl_3$, 500 MHz, 298 K): δ = 8.53 (d, J = 7.0 Hz, 4H), 8.03 (d, J = 8.0 Hz, 4H), 7.83 (dd, J_1 = 7.0, J_2 = 7.0 Hz, 4H), 7.51 (d, J = 8.0 Hz, 4H), 7.22 (dd, J_1 = 8.0, J_2 = 8.0 Hz, 4H), 7.02 ppm (d, J = 7.0 Hz, 4H); UV/Vis ($CHCl_3$): λ_{max} [nm] (ε [mol^{-1} dm^3 cm^{-1}]) = 563 (53000), 525 (55000).

Synthesis of 5: Benzo[*c*,*d*]indole-2(1*H*)-one (**lactam-1**, 170 mg, 1.0 mmol) and 2-aminopyridine (**amine-2**, 94 mg, 1.0 mmol) were dissolved in toluene (5.3 mL), and then TEA (2 mL) and $TiCl_4$ (0.2 mL) were added to the solution under reflux. After stirring for 15 min, $BF_3{\cdot}OEt_2$ (2.5 mL) was added, and the resulting mixture was further heated to reflux for 2 h. The reaction mixture was filtered, and the filtrate was added to water. The organic phase was extracted with chloroform and dried over Na_2SO_4. Finally the product was purified by silica gel column chromatography with chloroform as eluent and recrystallized from chloroform and hexane to afford **5** as a yellow powder in 5.2% yield (15 mg, 0.051 mmol). HR-MALDI-FT-ICR-MS: *m/z* 294.1009 (calcd for $C_{16}H_{11}BF_2N_3$: 294.1009 [M^++H]); ^{1}H NMR (CD_2Cl_2, 500 MHz, 298 K): δ = 8.43 (m, 1H), 8.26 (d, J = 7.0 Hz, 1H), 8.14 (d, J = 8.0 Hz, 1H), 8.00 (dd, J_1 = 8.0, J_2 = 8.0 Hz, 1H), 7.81 (dd, J_1 = 7.5, J_2 = 7.0 Hz, 1H), 7.70 (d, J = 8.0 Hz, 1H), 7.61 (dd, J_1 = 8.0, J_2 = 7.5 Hz, 1H), 7.55 (d, J = 8.0 Hz, 1H), 7.48 (d, J = 7.0 Hz, 1H), 7.28 ppm (dd, J_1 = 7.5, J_2 = 7.0 Hz, 1H); UV/Vis ($CHCl_3$): λ_{max} [nm] (ε [mol^{-1} dm^3 cm^{-1}]) = 468 (16000), 441 (24000).

Synthesis of 6: Benzo[*c*,*d*]indole-2(1*H*)-one (**lactam-1**, 0.34 g, 2.0 mmol) and 2-aminobenzooxazole (**amine-3**, 0.27 g, 2.0 mmol) were dissolved in toluene (10 mL), and then TEA (5 mL) and $TiCl_4$ (0.3 mL) were added to the solution under reflux. After stirring for 15 min, $BF_3{\cdot}OEt_2$ (4.4 mL) was added, and the resulting mixture was further heated to reflux for 2 h. The reaction mixture was filtered, and the filtrate was added to water. The organic phase was extracted with chloroform and dried over Na_2SO_4. Finally the product was purified by silica-gel column chromatography with chloroform as eluent and recrystallized from chloroform and methanol to afford **6** as a yellow powder in 4.3% yield (29 mg, 0.087 mmol). HR-MALDI-FT-ICR-MS: *m/z* 334.0958 (calcd for $C_{18}H_{11}BF_2N_3O$: 334.0958 [M^++H]); ^{1}H NMR ($CDCl_3$, 500 MHz, 298 K): δ = 8.41 (d, J = 7.0 Hz, 1H), 8.22 (d, J = 8.0 Hz, 1H), 7.82 (m, 4H), 7.68 (dd, J_1 = 7.5, J_2 = 7.0 Hz, 1H), 7.58 (d, J = 8.0 Hz, 1H), 7.49 ppm (m, 2H); UV/Vis ($CHCl_3$): λ_{max} [nm] (ε [mol^{-1} dm^3 cm^{-1}]) = 468 (8800), 436 (19000).

Synthesis of 7a: Benzo[*c*,*d*]indole-2(1*H*)-one (**lactam-1**, 85 mg, 0.50 mmol) and 2-aminobenzothiazole (**amine-4a**, 75 mg, 0.50 mmol) were dissolved in toluene (2 mL), and then TEA (1.4 mL) and $TiCl_4$ (0.08 mL) were added to the solution under reflux. After stirring for 15 min, $BF_3{\cdot}OEt_2$ (1.2 mL) was added, and the resulting mixture was further heated to reflux for 2 h. The reaction mixture was filtered, and the filtrate was added to water. The organic phase was extracted with chloroform and dried over Na_2SO_4. Finally the product was purified by silica-gel column chromatography with chloroform as eluent and recrystallized from chloroform and methanol to afford **7a** as a yellow powder in 16% yield (28 mg, 0.081 mmol). HR-MALDI-FT-ICR-MS: *m/z* 350.0729 (calcd for $C_{18}H_{11}BF_2N_3S$: 350.0729 [M^++H]); ^{1}H NMR ($CDCl_3$, 500 MHz, 298 K): δ = 8.35 (d, J = 7.0 Hz, 1H), 8.19 (d, J = 8.0 Hz, 1H), 8.17 (d, J = 8.0 Hz, 1H), 7.78 (m, 4H), 7.67 (dd, J_1 = 8.0, J_2 = 7.5 Hz, 1H), 7.59 (dd, J_1 = 8.0, J_2 = 7.0 Hz, 1H), 7.44 ppm (dd, J_1 = 8.0, J_2 = 7.5 Hz, 1H); UV/Vis ($CHCl_3$): λ_{max} [nm] (ε [mol^{-1} dm^3 cm^{-1}]) = 480 (16000), 450 (25000).

Synthesis of 7b: Benzo[*c*,*d*]indole-2(1*H*)-one (**lactam-1**, 61 mg, 0.36 mmol) and 2-amino-6-octyloxybenzothiazole (**amine-4b**, 100 mg, 0.36 mmol) were dissolved in toluene (1.3 mL), and then

TEA (0.75 mL) and $TiCl_4$ (0.04 mL) were added to the solution under reflux. After stirring for 15 min, $BF_3{\cdot}OEt_2$ (0.55 mL) was added, and the resulting mixture was further heated to reflux for 2 h. The reaction mixture was filtered, and the filtrate was added to water. The organic phase was extracted with chloroform and dried over Na_2SO_4. Finally the product was purified by silica-gel column chromatography with chloroform as eluent and recrystallized from chloroform and methanol to afford **7b** as a yellow powder in 5.9% yield (6.6 mg, 0.014 mmol). HR-MALDI-FT-ICR-MS: *m/z* 478.1931 (calcd for $C_{26}H_{27}BF_2N_3OS$: 478.1931 [M^++H]); ^{1}H NMR ($CDCl_3$, 500 MHz, 298 K): δ = 8.31 (d, J = 7.0 Hz, 1H), 8.16 (d, J = 8.0 Hz, 1H), 8.04 (d, J = 8.0 Hz, 1H), 7.81 (dd, J_1 = 8.0, J_2 = 7.0 Hz, 1H), 7.76 (d, J = 8.0 Hz, 1H), 7.72 (d, J = 7.0 Hz, 1H), 7.65 (dd, J_1 = 8.0, J_2 = 7.0 Hz, 1H), 7.22 (m, 2H), 4.03 (dd, J_1 = 6.5, J_2 = 6.5 Hz, 2H), 1.26 ppm (m, 15H); UV/Vis ($CHCl_3$): λ_{max} [nm] (ε [$mol^{-1}\,dm^3\,cm^{-1}$]) = 491 (24000), 461 (35000).

Synthesis of 8: Benzo[*c,d*]indole-2(1*H*)-one (**lactam-1**, 0.17 g, 1.0 mmol) and 2-aminoquinoline (**amine-5**, 0.14 g, 1.0 mmol) were dissolved in toluene (5.3 mL), and then TEA (2 mL) and $TiCl_4$ (0.2 mL) were added to the solution under reflux. After stirring for 30 min, $BF_3{\cdot}OEt_2$ (2.5 mL) was added, and the resulting mixture was further heated to reflux for 2 h. The reaction mixture was filtered, and the filtrate was added to water. The organic phase was extracted with chloroform and dried over Na_2SO_4. Finally the product was purified by silica-gel column chromatography with chloroform/MeOH (60/1) as eluent and recrystallized from chloroform and methanol to afford **8** as a yellow powder in 6.2% yield (16 mg, 0.047 mmol). HR-MALDI-FT-ICR-MS: *m/z* 344.1165 (calcd for $C_{20}H_{13}BF_2N_3$: 344.1165 [M^++H]); ^{1}H NMR ($CDCl_3$, 500 MHz, 298 K): δ = 8.83 (d, J = 8.5 Hz, 1H), 8.37 (d, J = 7.0 Hz, 1H), 8.22 (d, J = 8.5 Hz, 1H), 8.15 (d, J = 8.0 Hz, 1H), 7.82 (m, 3H), 7.73 (m, 2H), 7.65 (dd, J_1 = 7.0, J_2 = 7.0 Hz, 1H), 7.54 ppm (m, 2H); UV/Vis ($CHCl_3$): λ_{max} [nm] (ε [$mol^{-1}\,dm^3\,cm^{-1}$]) = 488 (24000), 458 (29000).

Synthesis of 9: Benzo[*c,d*]indole-2-amine (**amine-1**, 0.20 g, 1.2 mmol) and *2H*-1,4-benzoxazin-3(4*H*)-one (**lactam-2**, 0.15 g, 1.0 mmol) were dissolved in toluene (10 mL), and then TEA (2 mL) and $TiCl_4$ (0.2 mL) were added to the solution under reflux. After stirring for 30 min, $BF_3{\cdot}OEt_2$ (2.4 mL) was added, and the resulting mixture was further heated to reflux for 3.5 h. The reaction mixture was filtered, and the filtrate was added to water. The organic phase was extracted with chloroform and dried over Na_2SO_4. Finally the product was purified by silica-gel column chromatography with chloroform as eluent and recrystallized from chloroform and methanol to afford **9** as a yellow powder in 6.6% yield (23 mg, 0.066 mmol). HR-MALDI-FT-ICR-MS: *m/z* 348.1114 (calcd for $C_{19}H_{13}BF_2N_3O$: 348.1114 [M^++H]); ^{1}H NMR ([D_6]DMSO, 500 MHz, 298 K): δ = 8.51 (d, J = 8.0 Hz, 2H), 8.08 (d, J = 8.0 Hz, 1H), 8.02 (dd, J_1 = 7.5, J_2 = 7.5 Hz, 1H), 7.90 (d, J = 7.0 Hz, 1H), 7.80 (m, 2H), 7.20 (m, 3H), 5.16 ppm (s, 2H); UV/Vis ($CHCl_3$): λ_{max} [nm] (ε [$mol^{-1}\,dm^3\,cm^{-1}$]) = 484 (13000), 456 (21000).

Acknowledgements

This work was partly supported by Grants-in-Aid for Scientific Research on Innovative Area, "New Polymeric Materials Based on Element-Blocks (No. 25102503), from the Ministry of Education, Culture, Sports, Science and Technology (MEXT), Young Scientists A (No. 26708003) from Japan Society for the Promotion of Science (JSPS), and Bilateral Joint Research Program promoted by JSPS and National Research Foundation (NRF) of South Africa. The authors thank Prof. Takeaki Iwamoto, Dr. Shintaro Ishida, and Dr. Taniyuki Furuyama of Tohoku University for the X-ray measurements.

Keywords: aggregation · dyes/pigments · fluorescence · nitrogen heterocycles · solid-state emission

[1] a) A. Loudet, K. Burgess, *Chem. Rev.* **2007**, *107*, 4891–4932; b) A. Loudet, K. Burgess, in *Handbook of Porphyrin Science, Vol. 8* (Eds.: K. M. Kadish, K. M. Smith, R. Guilard), World Scientific Publishing, Singapore, **2010**, pp. 1–164.

[2] G. Ulrich, R. Ziessel, A. Harriman, *Angew. Chem. Int. Ed.* **2008**, *47*, 1184–1201; *Angew. Chem.* **2008**, *120*, 1202–1219.

[3] a) T. E. Wood, A. Thompson, *Chem. Rev.* **2007**, *107*, 1831–1861; b) T. E. Wood, M. I. Uddin, A. Thompson, in *Handbook of Porphyrin Science, Vol. 8* (Eds.: K. M. Kadish, K. M. Smith, R. Guilard), World Scientific Publishing, Singapore, **2010**, pp. 235–292.

[4] H. Lu, J. Mack, Y. Yang, Z. Shen, *Chem. Soc. Rev.* **2014**, *43*, 4778–4823.

[5] a) R. P. Haughland, *Handbook of Fluorescent Probes and Research Products*, Molecular Probes, Inc., Eugene, OR, **2002**; b) Y. Urano, D. Asanuma, Y. Hama, Y. Koyama, T. Barrett, M. Kamiya, T. Nagano, T. Watanabe, A. Hasegawa, P. L. Choyke, H. Kobayashi, *Nat. Med.* **2009**, *15*, 104–109.

[6] a) A. C. Benniston, G. Copley, *Phys. Chem. Chem. Phys.* **2009**, *11*, 4124–4131; b) N. Boens, V. Leen, W. Dehaen, *Chem. Soc. Rev.* **2012**, *41*, 1130–1172.

[7] a) A. Costela, I. García-Moreno, C. Gomez, R. Sastre, F. Amat-Guerri, M. Liras, F. López Arbeloa, J. Bañuelos Prieto, I. López Arbeloa, *J. Phys. Chem. A* **2002**, *106*, 7736–7742; b) D. Zhang, V. Martin, I. Garcia-Moreno, A. Costela, M. E. Perez-Ojeda, Y. Xiao, *Phys. Chem. Chem. Phys.* **2011**, *13*, 13026–13033.

[8] a) T. Yogo, Y. Urano, Y. Ishitsuka, F. Maniwa, T. Nagano, *J. Am. Chem. Soc.* **2005**, *127*, 12162–12163; b) S. Ozlem, E. U. Akkaya, *J. Am. Chem. Soc.* **2008**, *130*, 48–49.

[9] L. Bonardi, H. Kanaan, F. Camerel, P. Jolinat, P. Retailleau, R. Ziessel, *Adv. Funct. Mater.* **2008**, *18*, 401–413.

[10] a) S. Erten-Ela, M. D. Yilmaz, B. Icli, Y. Dede, S. Icli, E. U. Akkaya, *Org. Lett.* **2008**, *10*, 3299–3302; b) S. Kolemen, Y. Cakmak, S. Erten-Ela, Y. Altay, J. Brendel, M. Thelakkat, E. U. Akkaya, *Org. Lett.* **2010**, *12*, 3812–3815; c) D. Kumaresan, R. P. Thummel, T. Bura, G. Ulrich, R. Ziessel, *Chem. Eur. J.* **2009**, *15*, 6335–6339; d) Y. Hayashi, N. Obata, M. Tamaru, S. Yamaguchi, Y. Matsuo, A. Saeki, S. Seki, Y. Kureishi, S. Saito, S. Yamaguchi, H. Shinokubo, *Org. Lett.* **2012**, *14*, 866–869; e) S. Hattori, K. Ohkubo, Y. Urano, H. Sunahara, T. Nagano, Y. Wada, N. V. Tkachenko, H. Lemmetyinen, S. Fukuzumi, *J. Phys. Chem. A* **2005**, *109*, 15368–15375.

[11] D. Holten, D. F. Bocian, J. S. Lindsey, *Acc. Chem. Res.* **2001**, *34*, 57–69.

[12] a) A. Gorman, J. Killoran, C. O'Shea, T. Kenna, W. M. Gallagher, D. F. O'Shea, *J. Am. Chem. Soc.* **2004**, *126*, 10619–10631; b) W. Zhao, E. M. Carreira, *Angew. Chem. Int. Ed.* **2005**, *44*, 1677–1679; *Angew. Chem.* **2005**, *117*, 1705–1707; c) A. Díaz-Moscoso, E. Emond, D. L. Hughes, G. J. Tizzard, S. J. Coles, A. N. Cammidge, *J. Org. Chem.* **2014**, *79*, 8932–8936.

[13] a) A. Loudet, R. Bandichhor, K. Burgess, A. Palma, S. O. McDonnell, M. J. Hall, D. F. O'Shea, *Org. Lett.* **2008**, *10*, 4771–4774; b) J. Murtagh, D. O. Frimannsson, D. F. O'Shea, *Org. Lett.* **2009**, *11*, 5386–5389; c) A. Palma, M. Tasior, D. O. Frimannsson, T. T. Vu, R. Méallet-Renault, D. F. O'Shea, *Org. Lett.* **2009**, *11*, 3638–3641.

[14] V. F. Donyagina, S. Shimizu, N. Kobayashi, E. A. Lukyanets, *Tetrahedron Lett.* **2008**, *49*, 6152–6154.

[15] a) S. Shimizu, T. Iino, Y. Araki, N. Kobayashi, *Chem. Commun.* **2013**, *49*, 1621–1623; b) S. Shimizu, T. Iino, A. Saeki, S. Seki, N. Kobayashi, *Chem. Eur. J.* **2015**, *21*, 2893–2904.

[16] N. P. Vasilenko, F. A. Mikhailenko, *Ukr. Khim. Zh. (Ukr. Ed.)* **1986**, *52*, 308–311.

[17] N. P. Vasilenko, F. A. Mikhailenko, J. I. Rozhinsky, *Dyes Pigm.* **1981**, *2*, 231–237.

[18] During preparation of this manuscript, Jiao et al. also reported the synthesis of some of the benzo[*c,d*]indole-containing aza-BODIPYs in this paper. C. Cheng, N. Gao, C. Yu, Z. Wang, J. Wang, E. Hao, Y. Wei, X. Mu, Y. Tian, C. Ran, L. Jiao, *Org. Lett.* **2015**, *17*, 278–281.

[19] G. E. Ficken, J. D. Kendall, *J. Chem. Soc.* **1960**, 1537–1541.

[20] a) H. K. Hall, A. B. Padias, P. A. Williams, J. M. Gosau, H. W. Boone, D. K. Park, *Macromolecules* **1995**, *28*, 1 – 8; b) G. Nawn, S. R. Oakley, M. B. Majewski, R. McDonald, B. O. Patrick, R. G. Hicks, *Chem. Sci.* **2013**, *4*, 612 – 621.

[21] a) A. Wakamiya, K. Mori, S. Yamaguchi, *Angew. Chem. Int. Ed.* **2007**, *46*, 4273 – 4276; *Angew. Chem.* **2007**, *119*, 4351 – 4354; b) C.-H. Zhao, A. Wakamiya, Y. Inukai, S. Yamaguchi, *J. Am. Chem. Soc.* **2006**, *128*, 15934 – 15935.

[22] a) H. Liu, H. Lu, Z. Zhou, S. Shimizu, Z. Li, N. Kobayashi, Z. Shen, *Chem. Commun.* **2015**, *51*, 1713 – 1716; b) H. Liu, H. Lu, J. Xu, Z. Liu, Z. Li, J. Mack, Z. Shen, *Chem. Commun.* **2014**, *50*, 1074 – 1076.

[23] a) T. Ozdemir, S. Atilgan, I. Kutuk, L. T. Yildirim, A. Tulek, M. Bayindir, E. U. Akkaya, *Org. Lett.* **2009**, *11*, 2105 – 2107; b) H. Lu, Q. Wang, L. Gai, Z. Li, Y. Deng, X. Xiao, G. Lai, Z. Shen, *Chem. Eur. J.* **2012**, *18*, 7852 – 7861; c) Y. Kubota, J. Uehara, K. Funabiki, M. Ebihara, M. Matsui, *Tetrahedron Lett.* **2010**, *51*, 6195 – 6198; d) Y. Ooyama, Y. Hagiwara, Y. Oda, H. Fukuoka, J. Ohshita, *RSC Adv.* **2013**, *3*, 1163 – 1167.

[24] M. Kasha, H. R. Rawls, M. A. El-Bayoumi, *Pure Appl. Chem.* **1965**, *11*, 371 – 392.

[25] S. Choi, J. Bouffard, Y. Kim, *Chem. Sci.* **2014**, *5*, 751 – 755.

[26] U. Rösch, S. Yao, R. Wortmann, F. Würthner, *Angew. Chem. Int. Ed.* **2006**, *45*, 7026 – 7030; *Angew. Chem.* **2006**, *118*, 7184 – 7188.

[27] a) Y. Hong, J. W. Y. Lam, B. Z. Tang, *Chem. Soc. Rev.* **2011**, *40*, 5361 – 5388; b) Y. N. Hong, J. W. Y. Lam, B. Z. Tang, *Chem. Commun.* **2009**, 4332 – 4353.

[28] a) G. M. Sheldrick, SHELXL-97, Program for the Solution and Refinement of Crystal Structures, University of Göttingen, Göttingen, Germany, **1997**; b) Program for the refinement of crystal structures from diffraction data, University of Gottingen, Gottingen, Germany; G. M. Sheldrick, A short history of SHELX, *Acta Crystallogr. Sect. A* **2008**, *64*, 112 – 122.

[29] M. C. Burla, R. Caliandro, M. Camalli, B. Carrozzini, G. L. Cascarano, C. Giacovazzo, M. Mallamo, A. Mazzone, G. Polidori, R. Spagna, *J. Appl. Crystallogr.* **2012**, *45*, 357 – 361.

[30] Yadokari-XG, Software for Crystal Structure Analyses, K. Wakita, (2001); release of Software (Yadokari-XG 2009) for Crystal Structure Analyses, C. Kabuto, S. Akine, T. Nemoto, E. Kwon, *J. Cryst. Soc. Jpn.* **2009**, *51*, 218 – 224.

[31] Gaussian 09, Revision A.02, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, Gaussian, Inc., Wallingford CT, **2009**.

Received: April 15, 2015
Published online on July 17, 2015