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Xin-Dong Jiang, Jian Guan, Jiuli Zhao, Boris Le Guennic, Denis Jacquemin, et al.. Synthesis, structure and photophysical properties of NIR aza-BODIPYs with -F/-N-3/NH2 groups at 1,7-positions. Dyes and Pigments, 2017, 136, pp.619-626. 10.1016/j.dyepig.2016.09.019 . hal-01438101

HAL Id: hal-01438101 https://univ-rennes.hal.science/hal-01438101

Submitted on 18 May 2017 $\,$

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Synthesis, structure and photophysical properties of NIR aza-BODIPYs with –F/-N₃/-NH₂ groups at 1,7-positions

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Abstract: With 4-fluorostyrene as the starting material, symmetric/asymmetric fluorine-containing aza-difluoroboradiaza-*s*-indacenes (aza-BODIPYs) **3-6** at 1/7-position were successfully prepared. NaN₃ undertook nucleophilic aromatic substitution via replacement of F atoms of **4** to form the N₃/NH₂-containing aza-BODIPYs **9** and **10**. The solid-state structure of aza-BODIPY **4** was confirmed by single crystal X-ray analysis, the F-C_{Ph} bond distance of which was found to be shorter than those of the reported fluoride. These aza-BODIPYs absorb and emit in

the NIR region. Surprisingly, although the withdrawing group was introduced at 1/7 positions of **3-6**, the effect of the fluorine atoms to the photophysical properties is trifling. However, **9** and **10** with $-N_3/-NH_2$ groups resulted in a remarkable bathochromic shift. Aza-BODIPY **10** could be also used as a turn-on fluorescent probe for pH value. Moreover, the main photophysical data are well supported and explained by cLR-PCM(CHCl₃)-M06-2X/6-311+G(2d,p)/SOS-CIS(D) calculations.

Keywords: aza-BODIPY • NIR • fluorine • fluorescence • TD-DFT calculations

1. Introduction

Near-infrared (NIR) fluorescent dyes can greatly reduce background absorption, fluorescence, light scattering, and can be used as building blocks to improve the sensitivity of the probes and sensors [1]. More importantly, NIR fluorescent dyes with strong absorption and emission in the low energy regions (650-900 nm) have deep penetration in tissues which allows more efficient in vivo imaging and photodynamic therapy [2]. The safe, non-invasive nature of NIR fluorescent imaging has attracted great interests in the design and synthesis of novel NIR compounds [3]. Indeed, NIR derivatives such as azo, cyanine, quinone, and phthalocyanine dyes have been developed though, in most cases, insufficient photo-stability and/or difficult modification obstructed their applications [3]. Most NIR fluorescent dyes possess highly π -conjugated systems which lead to significantly reduced fluorescence quantum yields due to increased internal conversion. However, BODIPY and their derivatives are well-known to be highly fluorescent and very stable dyes, presenting tunable emission wavelengths and an exceptional insensitivity to the polarity of the medium [4]. Therefore, they are very promising candidates for biological labeling applications, and are already used in those fields [4,5].

By using an imine instead of a methane in BODIPY system to narrow the HOMO-LUMO gap one obtains aza-BODIPY that are known to be an attractive platform to reach NIR absorption (Fig. 1a) [6]. Furthermore, by introducing an electron-donating/withdrawing group one can further reduce the HOMO-LUMO gap by increasing the HOMO and/or decreasing the LUMO energy and reach more redshifted absorption and emission bands [7]. For instance, aza-BODIPYs with an electron-donating group such as -(p-NMe₂)Ph/-(p-OMe)Ph at 3/5-positions (Fig. 1b) exhibit bathochromic shift of the absorption/emission bands [8]. By contrast, aza-BODIPYs bearing an electron-withdrawing group (such as the -CN group) at 1/7-positions (Fig. 1c) are also known to undergo a redshift of the absorption/emission bands [9]. Since fluorine is a strong inductive acceptor, introduction of fluorine atom(s) in aza-BODIPY was considered in the present work. Importantly, the introduction of a fluorine atom into an organic molecule often induces significant, if not remarkable, variations of its chemical, physical and biological properties, due to the lipophilizing nature, strong electron-withdrawing nature and specific steric repulsion of fluorine [10]. In line with their widespread use in both medicinal chemistry and in materials science, fluorinated molecules have attracted a considerable interest in the framework of molecular design. Therefore, studies on the characteristic of a fluorine-containing aza-BODIPY at 1/7-positions are of importance. We have been already exploring fluorides [11], and our most recent research interest lies in novel BODIPY/aza-BODIPY family of fluorescent dyes [12].

<Fig. 1>

2. Experimental methods

2.1 General: The melting points were measured using a SGW® X-4 melting point apparatus. ¹H NMR spectra were recorded on a Bruker AVANCE III 500 MHz spectrometer. ¹H NMR chemical shifts (δ) are given in ppm downfield from Me₄Si, determined by chloroform (δ = 7.26 ppm). ¹³C NMR spectra were recorded on a Bruker AVANCE III 125 MHz spectrometer. ¹³C NMR chemical shifts (δ) are reported in ppm with the internal CDCl₃ at δ 77.0 ppm as standard. HRMS (ESI) was measured by micro TOF-Q II.

Tetrahydrofuran (THF) was freshly distilled from Na/benzophenone, *n*-hexane was distilled over Na, and other solvents were distilled over CaH₂. Merck silica gel 60 was used for the column chromatography. Fluorescence spectra were recorded on F-4600 spectrophotometer. UV/Vis spectra were recorded on UV-2550 spectrophotometer at room temperature. The refractive index of the medium was measured by 2 W Abbe's refractometer at 20 °C. The fluorescence quantum yields (Φ_f) of the BODIPY systems were calculated using the following relationship (equation 1):

$$\Phi_{\rm f} = \Phi_{\rm ref} F_{\rm sampl} A_{\rm ref} n^2_{\rm sampl} / F_{\rm ref} A_{\rm sampl} n^2_{\rm ref}$$
(1)

Here, *F* denotes the integral of the corrected fluorescence spectrum, *A* is the absorbance at the excitation wavelength, ref and sampl denote parameters from the reference and unknown experimental samples, respectively. The reference systems used was boronazadipyrromethene dye [13] as standard ($\Phi_{\rm f} = 0.36$ in chloroform, $\lambda_{\rm abs} = 688$ nm) for 3-6, 9 and 10.

2.2 Computational details: DFT, and TD-DFT calculations on molecules were carried out with the latest version of the Gaussian 09 program package [14], applying both a tightened self-consistent field convergence criterion $(10^{-9}-10^{-10} \text{ au})$ and an improved optimization threshold $(10^{-5} \text{ au} \text{ on average forces})$. For each molecule, we have optimized the geometry of both the ground and the first excited states, as well as computed the vibrational spectra of both states. The same DFT integration grid, namely the so-called ultrafine pruned (99,590) grid, was used for both the ground and excited states. All DFT and TD-DFT calculations were performed with the M06-2X hybrid exchange–correlation functional, that has been shown to be an adequate choice for investigating excited-state energies and structures of many classes of molecules [15]. Atoms were described with the 6-311+G(2d,p) basis sets. Solvation effects (here CHCl₃) have been quantified using the Polarizable Continuum Model (PCM) [16].

Here, we have applied the corrected LR approach [17]. The SOS-CIS(D)/6-311+G(2d,p) energies were determined with the Q-Chem package using the resolution of identity (RI) scheme with the same basis set. The interested reader can find the whole applied computational protocol in ref. 18.

Synthesis of 1-Fluoro-4-(1,2-dibromoethyl)benzene: Under N₂, Br₂ (0.42 ml, 8.1 mmol) in CH₂Cl₂ (20 ml) was dropwise added to 4-fluorostyrene (1.0 g, 8.1 mmol) in CH₂Cl₂ (40 ml) at 0 °C for 30 min. The color of the mixture changed from red to colorless. The reaction was allowed to warm up to room temperature slowly. After removal of the solvents by evaporation, the resulting crude mixture was recrystallization (*n*-hexane) to afford 1-fluoro-4-(1,2-dibromoethyl)benzene (1.82 g, 80%) as yellow solids.

2.3 Synthesis

Synthesis of 3-(4-fluorophenyl)-2*H*-azirine: Under N₂, NaN₃ (840 mg, 12.9 mmol) was slowly added to 1-fluoro-4-(1,2-dibromoethyl)benzene (1.8 g, 6.3 mmol) in DMSO (20 ml) at 20 °C and stirred for 12 h at 25 °C. Then, 50% NaOH (1 ml) was added to the mixture and stirred for 24 h at 25 °C. The reaction was quenched with 10% NaHCO₃ (50 ml). The mixture was extracted with CH₂Cl₂ (2 × 30 ml), and the organic layer was washed with brine (2 × 30 ml) and dried over anhydrous MgSO₄. After removal of the solvents by evaporation, the red oil was obtained. Toluene (40 ml) was added the red oil and the mixture was refluxed for 2 h. After removal of the solvents by evaporating crude mixture was separated by column chromatography (*n*-hexane : CH₂Cl₂ = 1 : 1) to afford 3-(4-fluorophenyl)-2*H*-azirine (510 mg, 60%) as yellow oil. This mixture was direct used for the next step without further purification. ¹H NMR (500 MHz, CDCl₃): δ (ppm) 7.22-7.25 (m, 2H), 7.13-7.17 (m, 2H), 2.34 (s, 2H).

Synthesis of pyrrole 1: Under N₂, 1-tetralone (71.0 mg, 0.59 mmol) in DMSO (10 ml) was added to NaH (excess) in DMSO (10 ml) at -40 °C and stirred for 10 min. Then, 3-(4-fluorophenyl)-2*H*-azirine (80 mg, 0.59 mmol) in DMSO (5 ml) was added and the resulting mixture was stirred for 1 h at the same temperature. The reaction was allowed to warm up to room temperature slowly. It was quenched with water, neutralized with dilute HCl to a pH about 7. The mixture was extracted with CH₂Cl₂ (2 × 30 ml), and the organic layer was washed with brine (2 × 30 ml) and dried over anhydrous MgSO₄. After removal of the solvents by evaporation, the resulting crude mixture was separated by column chromatography (*n*-hexane : CH₂Cl₂ = 1 : 1) to afford pyrrole **1** as hoary solids (76.9 mg, 55%). ¹H NMR (500 MHz, CDCl₃): δ (ppm) 8.45 (br s, 1H), 7.50-7.53 (m, 4H), 7.40 (t, ³J = 8.0 Hz, 2H), 7.25 (d, ³J = 7.5 Hz, 1H), 7.80-7.09 (m, 1H), 7.05 (t, ³J = 8.5 Hz, 2H), 6.76 (m, 1H). HRMS-MALDI (m/z): [M + H]⁺ calcd for C₁₆H₁₃FN: 238.10265; found: 238.10268.

Synthesis of pyrrole 2: 6-Methoxytetralone (218 mg, 1.45 mmol) was used as the starting materials, and pyrrole **2** was obtained green solids (232.8 mg, 60%). ¹H NMR

(500 MHz, CDCl₃): δ (ppm) 8.34 (br s, 1H), 7.51 (d, ${}^{3}J = 9.0$ Hz, 1H), 7.50 (d, ${}^{3}J = 9.0$ Hz, 1H), 7.44 (d, ${}^{3}J = 9.0$ Hz, 2H), 7.02-7.06 (m, 3H), 6.94 (d, ${}^{3}J = 8.5$ Hz, 2H), 6.65 (m, 1H), 3.84 (s, 1H). HRMS-MALDI (m/z): [M + H]⁺ calcd for C₁₇H₁₅FNO: 268.11322; found: 268.11322.

Synthesis of aza-BODIPY 3: Sodium nitrite (6.9 mg, 0.1 mmol) was added to a suspension of pyrrole 1 (47.5 mg, 0.2 mmol) in a mixture of acetic acid/anhydride (1 ml/0.4 ml) at 0 °C, and was stirred for 10 min. The color changed from colorless to brown, then green, and finally dark green was observed. After 0.5 h stirring at room temperature, the mixture was heated at 80 °C for 0.5 h. Crushed ice was added to the mixture, the resulted dark green dye was filtered, washed with water. The dark green dye was dissolved in CH₂Cl₂, filtered through a pad of alumina (activity III). Solvent was removed under reduced pressure, and the residue was dissolved in dry 1,2-dichloroethane. Triethylamine (0.28 ml, 2.0 mmol) was added, followed by dropwise addition of BF₃·Et₂O (0.50 ml, 4.0 mmol) with stirring at room temperature. The mixture was stirred for 0.5 h, then heated in 80 °C for 0.5 h. The reaction was quenched with crushed ice, extracted with CH₂Cl₂, and purified by chromatography on silica gel followed by recrystallization from CH₂Cl₂/n-hexane to afford aza-BODIPY 3 (24.5 mg, 46%) as coppery solids. M.p.: 240.0-240.8 °C (decomp.). ¹H NMR (500 MHz, CDCl₃) ¹H NMR (500 MHz, CDCl₃): δ (ppm) 8.02-8.04 (m, 8H), 7.48-7.50 (m, 6H), 7.16 (t, ${}^{3}J$ = 8.5 Hz, 4H). 13 C NMR (125 MHz, CDCl₃): δ (ppm) 159.6, 145.4, 143.0, 131.4, 131.2, 131.1, 131.0, 129.5, 128.6, 118.8, 115.8, 115.7. HRMS-MALDI (m/z): $[M + Na]^+$ calcd for $C_{32}H_{20}BF_4N_3Na$: 556.1584; found: 556.1583.

Synthesis of aza-BODIPY 4: Pyrrole **2** (53.6 mg, 0.2 mmol) was used as the starting materials, and aza-BODIPY **4** was obtained green solids (25.5 mg, 43%). M.p.: 290.0–291.0 °C (decomp.). ¹H NMR (500 MHz, CDCl₃): δ (ppm) 8.08 (d, ³*J* = 8.5 Hz, 4H), 8.01 (dd, ³*J* = 8.5 Hz, 4H), 7.14 (t, ³*J* = 8.5 Hz, 4H), 7.01 (d, ³*J* = 8.5 Hz, 4H), 6.99 (s, 2H), 3.89 (s, 6H). ¹³C NMR (125 MHz, CDCl₃): δ (ppm) 161.9, 158.1, 145.1, 141.9, 131.6, 131.0, 128.6, 123.9, 118.3, 115.7, 115.5, 114.2. HRMS-MALDI (m/z): [M + H]⁺ calcd for C₃₄H₂₅BF₄N₃O₂: 594.19705; found: 594.19678.

Synthesis of aza-BODIPY 5: Sodium nitrite (11.6 mg, 0.16 mmol) was added to a suspension of 2,4-diphenyl-1*H*-pyrrole (36.9 mg, 0.16 mmol) in acetic acid (1 mL) at 0 °C, and was stirred for 10 min. The color changed from colorless to brown, then green, and finally brown was observed. The second pyrrole moiety **1** (40 mg, 0.16 mmol) was added, followed by addition of acetic anhydride (0.4 mL). The mixture turned blue immediately. After 0.5 h stirring, the mixture was heated at 80 °C for 0.5 h. Crushed ice was added to the mixture, the resulted blue dye was filtered, washed with water. The blue dye was dissolved in CH_2Cl_2 , filtered through a pad of alumina (activity III). Solvent was removed under reduced pressure, and the residue was dissolved in dry 1,2-dichloroethane. Triethylamine (0.28 mL, 2.0 mmol) was added, followed by dropwise addition of $BF_3 \cdot Et_2O$ (0.50 mL, 4.0 mmol) with stirring at room temperature. The mixture was stirred for 0.5 h, then heated in 80 °C for 0.5 h. The

reaction was quenched with crushed ice, extracted with CH₂Cl₂, and purified by chromatography on silica gel followed by recrystallization from CH₂Cl₂/*n*-hexane to afford aza-BODIPY **5** (42.0 mg, 51%) as coppery solids. M.p.: 230–231.0 °C (decomp.). ¹H NMR (500 MHz, CDCl₃): δ (ppm) 8.01-8.07 (m, 8H), 7.46-7.49 (m, 9H), 7.14 (t, (t, ³*J* = 8.5 Hz, 2H), 7.04 (s, 1H), 6.98 (s, 1H). ¹³C NMR (125 MHz, CDCl₃): δ (ppm) 159.6, 159.3, 145.5, 145.3, 144.2, 142.8, 132.1, 131.4, 131.2, 131.1, 131.0, 130.9, 129.6, 129.5, 129.4, 129.3, 129.2, 128.6, 128.5, 126.4, 119.2, 118.6, 115.7, 115.6. HRMS-MALDI (m/z): [M + H]⁺ calcd for C₃₂H₂₂BF₃N₃: 516.18534; found: 516.18463.

Synthesis of aza-BODIPY 6: 2-(4-methoxyphenyl)-4-phenyl-1H-pyrrole (25.0 mg, 0.093 mmol) and pyrrole **2** (24.1 mg, 0.096 mmol) was used as the starting materials, and aza-BODIPY **6** was obtained green solids (26.2 mg, 49%). M.p.: 257.0–258.0 °C (decomp.). ¹H NMR (500 MHz, CDCl₃): δ (ppm) 8.01-8.10 (m, 8H), 7.41-7.48 (m, 3H), 7.13 (t, ³*J* = 8.5 Hz, 2H), 7.04 (s, 1H), 7.01 (dd, ³*J* = 8.5 Hz, ⁴*J* = 3.0 Hz, 4 H), 6.98 (s, 1H), 3.89 (s, 3H), 3.88 (s, 3H). ¹³C NMR (125 MHz, CDCl₃): δ (ppm) 161.8, 158.2, 158.0, 157.9, 145.2, 145.1, 143.2, 141.7, 132.4, 131.5, 131.0, 130.9, 129.3, 129.2, 128.6, 128.5, 124.1, 123.9, 118.7, 118.6, 118.1, 115.6, 115.5, 114.2. HRMS-MALDI (m/z): [M + Na]⁺ calcd for C₃₄H₂₅BF₃N₃NaO₂: 598.1890; found: 598.1889.

Synthesis of aza-BODIPY 9: NaN₃ (8.8 mg, 0.13 mmol) was added to a solution of 4 (25.0 mg, 0.042 mmol) in DMF (4 ml), and then the mixture was stirred at 40 °C for 30 min. The reaction was quenched with water, extracted with CH₂Cl₂, and purified by chromatography on silica gel followed by recrystallization from CH₂Cl₂/*n*-hexane to afford aza-BODIPY 9 (15.3 mg, 57%) as coppery solids. ¹H NMR (500 MHz, CDCl₃): δ (ppm) 8.04 (d, ³J = 8.5 Hz, 4H), 7.79 (d, ³J = 8.5 Hz, 4H), 6.99 (d, ³J = 8.5 Hz, 4H), 6.85 (s, 2H), 6.75 (d, ³J = 8.5 Hz, 4H), 3.87 (s, 6H). HRMS-MALDI (m/z): [M - 4N + 5H]⁺ calcd for C₃₄H₂₉BF₂N₅O₂: 588.23769; found: 588.23730.

Synthesis of aza-BODIPY 10: NaN₃ (3.0 mg, 0.046 mmol) was added to a solution of 4 (27.4 mg, 0.046 mmol) in DMF (5 ml), and then the mixture was stirred at 40 °C for 1 h. The reaction The reaction was quenched with NaHS aqueous solution, extracted with CH₂Cl₂, and purified by chromatography on silica gel followed by recrystallization from CH₂Cl₂/*n*-hexane to afford aza-BODIPY 10 (13.5 mg, 50%) as coppery solids. ¹H NMR (500 MHz, CDCl₃): δ (ppm) 8.08 (d, ³*J* = 8.5 Hz, 2H), 8.03 (td, ³*J* = 8.5 Hz, ⁴*J* = 3.0 Hz, 4H), 7.96 (d, ³*J* = 8.5 Hz, 2H), 7.15 (t, ³*J* = 8.5 Hz, 2H), 7.00 (dd, ³*J* = 8.5 Hz, ⁴*J* = 3.0 Hz, 4H), 6.92 (s, 1H), 6.90 (s, 1H), 6.74 (d, ³*J* = 8.5 Hz, 2H), 4.04 (br s, 2H), 3.88 (s, 6H). HRMS-MALDI (m/z): [M + H]⁺ calcd for C₃₄H₂₇BF₃N₄O₂: 591.21737; found: 591.21777.

3. Results and Discussion

To introduce the fluorine atom into the aza-BODIPY core, 4-fluorostyrene was selected as a starting material (Scheme 1). 1-Fluoro-4-(1,2-dibromoethyl)benzene was obtained in 80% yield by the reaction of 4-fluorostyrene with Br₂ at 0 °C. Followed the NaN₃, DMSO, NaOH and reflux in toluene, bv vellow oil 3-(4-fluorophenyl)-2H-azirine can be synthesized in 60% yield. Acetophenone was employed to react with 3-(4-fluorophenyl)-2H-azirine to give fluoro-containing pyrroles 1 (y. 55%) and 2 (y. 60%) in the presence of NaH (Scheme 1), respectively [19]. The clear 1:10 integral areas of the hydrogen signals in pyrrole 2 between the proton of N-H (δ = 8.34 (br s, 1H)) and other protons of the pyrrole in the ¹H NMR spectrum were obtained (see ESI), indicating that the fluorine atom was successfully introduced into the pyrrole skeleton.

<Scheme 1>

<Scheme 2>

Using the pyrroles 1 and 2, symmetric/asymmetric fluorine-containing aza-BODIPYs 3-6 were successfully synthesized in moderate yields under HOAc, Ac₂O and NaNO₂, followed by complexation with Et_3N -BF₃ · Et₂O, as described in the literature (Scheme 2) [19]. Their structures were unambiguously confirmed by detailed characterizations including NMR and ESI-HRMS analyses (see ESI).

Furthermore, the solid-state structure of aza-BODIPY **4** was clearly confirmed by single crystal X-ray analysis (Fig. 2 and see ESI). Selected bond lengths and angles are summarized in Fig. 2. The F2-C15 distances (1.278 Å) were found to be slightly shorter than the F-C_{Ph} bond of the reported fluoride (1.365 Å) by 0.09 Å [11c]. The other bond lengths for **4** are very similar to those found for **8** (R₁ = H, R₂ = OMe) (Fig. 1b) [13]. Additionally, the *sp*³ hybridized boron center for **4** appears as a slightly distorted tetrahedron with angles. The dihedral angles C(11*)-N(2)-C(11)-C(10) of 179.9° are nearly of the ideal value of 180°, thus indicating the plane skeleton of the aza-BODIPY core.

<Fig. 2>

Additionally, the derivative of the fluorine-containing aza-BODIPYs was found to be feasible (Scheme 3). NaN₃ undertook nucleophilic aromatic substitution (SN_{Ar}) via replacement of the fluorine atoms of **4** to form N₃-containing aza-BODIPY **9** by treatment of water, whereas it provides NH₂-containing aza-BODIPY **10** by treatment of NaHS (Scheme 3) [20]. The proton of N- H_2 (δ = 4.04 (br s, 2H)) and other distinct hydrogen signals for the asymmetric NH₂-containing aza-BODIPY **10** in the ¹H NMR spectrum indicate clearly that the amino group was introduced into the aza-BODIPY **10** (see ESI).

<Scheme 3>

<Table 1>

The absorption and emission spectra of aza-BODIPYs **3-6** are shown in Fig. 3 whereas the photophysical data collected are listed in Table 1. Aza-BODIPYs **3-6**

have excellent optical properties. These dyes absorb and emit in the NIR region, with high molar extinction coefficients, high quantum yields and narrow full width at half maxima (FWHM). The profile curves including absorption and emission between 3/4 and 5/6 nearly overlap, and optical properties of every pair of aza-BODIPYs are very similar. Moreover, the pictures of 3-6 taken in CHCl₃ under normal conditions reveal vivid colors, and the hues between pairs of 3/4 and 5/6 are also uniform (Fig. 3). To investigate the spectroscopic effects of the withdrawing group F atom, the spectral characteristics of 3-6 were respectively compared to those of the known dyes 7 (R₁ = R₂ = H) [13] and 8 [13] (Fig. 1b and Table 1). By comparison with the absorption and emission maxima of 7 ($\lambda_{abs} = 650$, $\lambda_{em} = 672$ nm), *it is clear that the effect of the fluorine atom in 3 and 5 is trifling.* Moreover, extinction coefficients and quantum yields of dyes 3 and 5 in CHCl₃ are nearly the same to those of dye 7 (79000 M⁻¹ cm⁻¹, $\Phi_f = 0.34$). In addition, the photophysical properties of mono/bis-fluoro substituted aza-BODIPYs 4 and 6 bearing the –OMe group are also completely equivalent to those of aza-BODIPY 8.

<Fig. 3>

Interestingly, the replacement of -F atoms with -N₃ groups in **9** ($\lambda_{abs} = 710$ nm) resulted in a remarkable bathochromic shift (22 nm) compared to that of the parent aza-BODIPY **4** ($\lambda_{abs} = 688$) (Fig. 4 and Table 1), which is well in agreement with the reported literature [9]. Although the electronegativity of N₃ group (-3.04) was well-known to be smaller than that of F atom (-4.0) [18], the effect of the N₃ group at 1/7 position to photophysical properties in aza-BODIPY **9** is notable (Fig. 4 and Table 1), comparing to F-containing aza-BODIPYs **3-6** as described above. Aza-BODIPY **9** emits at 754 nm, possesses large Stokes' shift (44 nm) and has moderate quantum yield ($\Phi_f = 0.26$). The absorption and emission maxima of **10** bearing the NH₂-donating group ($\lambda_{abs} = 688$ nm, $\lambda_{em} = 715$ nm), and the fluorescence of **10** became so weak (0.03) due to the intramolecular charge transfer (ICT) effect.

<Fig. 4>

Since having a $-NH_2$ group in **10**, therefore, we continued to explore the response of the amino-containing aza-BODIPY **10** to pH value. Dimethylamino group (-NMe₂) is well-known to be one of the fragments for the pH-responsive fluorescent probe frequently used for the purpose of the ICT effect.[21] In this ICT process, the excited state of the fluorophore can be quenched by the electron transfer from electron donating amine to the fluorophore; upon recognition of a proton, the electron transfer is "switched off" and in turn the emission of fluorescence is "switched on". Herein, the mechanism of aza-BODIPY **10** bearing a $-NH_2$ group to pH value is same to that of the above description. Upon addition of hydrochloric acid to **10** with a $-NH_2$ group as the pH-sensitive functionality, **10** was protonated at relatively low pH value [8,22], and a distinctly hypochromatic shift accurs at pH 2 (Fig. 5a). A stepwise increase of the absorption intensity was observed in the 700 nm band of **10-H**⁺ from the 710 nm of **10** in DMSO/H₂O (2:1, v/v) (Fig. 5a). The absorption intensity of **10-H**⁺ reached the maximum when 4 M HCl was used. The absorption band of **10-H**⁺ is blue-shifted by about 10 nm compared to that of **10**. Furthermore, with decreasing pH, a remarkable increase in fluorescence intensity at 750 nm by about 6 folds when **10** was treated with 4M HCl. (Fig. 5b). So, aza-BODIPY **10** could be used as a turn-on fluorescent probe for pH value.

<Fig. 5>

Quantum chemical calculations were performed on the four fluorine-containing aza-BODIPY compounds 3-6 to support the absorption and emission results. We followed a strategy that was developed recently (see computational details) [23] and that gave excellent result for both the BODIPY and aza-BODIPY systems [24]. The main computed photophysical data at the best level of calculation, i.e. cLR-PCM(CHCl₃)-M06-2X/6-311+G(2d,p)/SOS-CIS(D) are summarized in Table 2. The calculations confirmed the limited effect of adding a F atom at 1/7-positions, comparing for instance the calculated absorption and emission wavelengths of 4 and 6 with respect to those of 8. This observation persists for the absoprtion/fluorescence crossing point energies (E^{AFCP}) that can be compared to experimental E^{0-0} energies. Fig. 6 shows the density difference plots computed for the fluorine-containing aza-BODIPY dyes and the involvement of the fluorine atom is clearly limited in the excited-states, which is consistent with the measurements. CT parameters, i.e. the CT distance (d^{CT}) and the transferred charge (q^{CT}) were also calculated through Le Bahers' model (Table 2) [25]. Again the only substantial difference emerges when comparing CT distances of parent complexes with and without the methoxy group (3 vs. 4 for instance). Similar calculations were realized on compounds 9 and 10 (Table 2 and Fig. 6) confirming the tendencies experimentally observed, such as the redshift of the absorption/emission when going from 3 and 4 to 9 and 10. Replacing F by N_3 (4 vs. 9) slightly reduces the CT distance in agreement with the smaller electronegativity of N₃ with respect to F. Finally, the small calculated d^{CT} of **10** can be attributed to the strong dissymmetry induced by the replacement of only one fluorine group by NH₂ donating group.

<Table 2> <Fig. 6>

4. Conclusions

Utilizing 4-fluorostyrene as starting material, acetophenone was employed to react with 3-(4-fluorophenyl)-2*H*-azirine to give fluoro-containing pyrroles in the presence

of NaH. Fluorine-containing aza-BODIPYs 3-6 at 1/7-position were successfully synthesized by the reaction of fluoro-containing pyrroles 1 and 2 under HOAc, Ac_2O and NaNO₂, followed by complexation with Et₃N-BF₃ · Et₂O. NaN₃ undertook nucleophilic aromatic substitution to form N_3 -containing aza-BODIPY 9 by treatment of water, whereas it gives NH_2 -containing aza-BODIPY 10 by treatment of NaHS. The solid-state structure of aza-BODIPY 4 was confirmed by single crystal X-ray analysis, the F-C_{Ph} bond distance of which was found to be shorter than those of the reported fluoride. The optical properties of fluorine-containing aza-BODIPYs 3-6 are very similar to those of the parent complexes. Surprisingly, the effect of the withdrawing -F group at 1/7-position on the photophysical properties is found to be almost negligible, comparing to those of the parent aza-BODIPYs 7 and 8. However, the replacement of -F atoms with -N₃/-NH₂ groups in 9 and 10 resulted in a remarkable bathochromic shift. The amino-containing aza-BODIPY 10 could be used as a turn-on fluorescent probe for pH value. The main photophysical data are well supported and explained by cLR-PCM(CHCl₃)-M06-2X/6-311+G(2d,p)/SOS-CIS(D) calculations.

Acknowledgements

This work was supported by NNSFC (21542004), the Program for Liaoning Excellent Talents in University (LJQ2015087), Liaoning BaiQianWan Talents Program (2015-56), the State Key Laboratory of Fine Chemicals (KF1506), the Public Research Foundation of Liaoning Province for the Cause of Science (2014003009), the Scientific Research Foundation for the Returned Overseas Chinese Scholars, Liaoning Province Natural Science Foundation (2014020139), and the start-up funds from Shenyang University of Chemical Technology. D.J. acknowledges the European Research Council (ERC) and the Région des Pays de la Loire for financial support in the framework of a Starting Grant (Marches-278845) and a recrutement sur poste stratégique, respectively. This research used resources of (i) the GENCI-CINES/IDRIS, (ii) the CCIPL (Centre de Calcul Intensif des Pays de Loire), and (iii) the Troy cluster in Nantes.

References

- (a) Weissleder R. A clearer vision for in vivo imaging. Nat Biotechnol 2001;19:316.
 - (b) Tung CH, Lin Y, Moon WK, Weissleder R. A receptor-targeted near-infrared fluorescence probe for in vivo tumor imaging. ChemBioChem 2002;3:784.
 - (c) Kim HN, Ren W, Kim JS, Yoon J. Fluorescent and colorimetric sensors for detection of lead, cadmium, and mercury ions. Chem Soc Rev 2012;41:3210.
 - (d) Joseph R, Rao CP. Ion and molecular recognition by lower rim 1,3-diconjugates of calix[4]arene as receptors. Chem Rev 2011;111:4658.
 - (e) Liu Z, He W, Guo Z. Metal coordination in photoluminescent sensing. Chem

Soc Rev 2013;42:1568.

(f) Ding Y, Tang Y, Zhu W, Xie Y. Fluorescent and colorimetric ion probes based on conjugated oligopyrroles. Chem Soc Rev 2015;44:1101.

[2] (a) Weissleder R, Tung CH, Mahmood U, Bogdanov A, In vivo imaging of tumors with protease-activated near-infrared fluorescent probes. Nat Biotechnol 1999;17:375.

(b) Becker A, Hessenius C, Licha K, Ebert B, Sukowski U, Semmler W, et al. Receptor-targeted optical imaging of tumors with near-infrared fluorescent ligands. Nat Biotechnol 2001;19:327.

- [3] (a) Li Y, Patrick BO, Dolphin D. Near-Infrared absorbing azo dyes: synthesis and X-ray crystallographic and spectral characterization of monoazopyrroles, bisazopyrroles, and a boron-azopyrrole complex. J Org Chem 2009;74:5237.
 - (b) Descalzo AB, Rurack K. On the signalling pathways and Cu(II)-mediated anion indication of N-meso-substituted heptamethine cyanine dyes. Chem Eur J 2009;15:3173.
 - (c) Kubo Y, Yoshida K, Adachi M, Nakamura S, Maeda S. Experimental and theoretical study of near-infrared absorbing naphthoquinone methide dyes with a nonplanar geometry. J Am Chem Soc 1991;113:2868.
 - (d) Barthram AM, Cleary RL, Kowallick R, Ward MD. A new redox-tunable near-IR dye based on a trinuclear ruthenium(II) complex of hexahydroxytriphenylene. Chem Commun 1998;2695.
 - (e) Hairong L, Ngan N, Frank RF. Syntheses and properties of octa-, tetra-, and di-hydroxy-substituted phthalocyanines. Tetrahedron 2009;65:3357.
 - (f) Fan J, Dong H, Hu M, Wang J, Zhang H, Zhu H, et al. Fluorescence imaging lysosomal changes during cell division and apoptosis observed using Nile Blue based near-infrared emission. Chem Commun 2014;50:882.
 - (g) Zhao C, Zhang J, Wang X, Zhang Y. Pyridone fused boron-dipyrromethenes: synthesis and properties. Org Biomol Chem 2013;11:372.
 - (h) Miao JT, Fan C, Shi XY, Sun R, Xu YJ, Ge JF. Colorimetric and ratiometric pH responses by the protonation of phenolate within hemicyanine. Analyst 2014;139:6290.
- [4] (a) Rohrer H, Hofmann W. Versuche zur acktiven Immunisierung bei Maul- und Klauenseuche mit Mäusegehirnpassagevirus vom B-Typ. Nature 1943;151:504.
 - (b) Loudet A, Burgess K. BODIPY dyes and their derivatives: syntheses and spectroscopic properties. Chem Rev 2007;107:4891.
 - (c) Bessette A, Hanan GS. Design, synthesis and photophysical studies of dipyrromethene-based materials: insights into their applications in organic photovoltaic devices. Chem Soc Rev 2014;43:3342.
 - (d) Jiao L, Wu Y, Ding Y, Wang S, Zhang P, Yu C, et al. Conformationally restricted aza-dipyrromethene boron difluorides (aza-BODIPYs) with high fluorescent quantum yields. Chem Asian J 2014;9:805.

(e) Killoran J, O'Shea DF. Impact of a conformationally restricted receptor on the BF_2 chelated azadipyrromethene fluorosensing platform. Chem Commun 2006;1503.

(f) McDonnell SO, Hall MJ, Allen LT, Byrne A, Gallagher WM, O'Shea DF. Supramolecular Photonic Therapeutic Agents. J Am Chem Soc 2005;127:16360.

(g) Hall MJ, Allen LT, O'Shea DF. PET modulated fluorescent sensing from the BF_2 chelated azadipyrromethene platform. Org Biomol Chem 2006;4:776.

(h) Adarsh N, Krishnan MS, Ramaiah D. Sensitive naked eye detection of hydrogen sulfide and nitric oxide by aza-BODIPY dyes in aqueous medium. Anal Chem 2014;86:9335.

- [5] (a) Umezawa K, Nakamura Y, Makino H, Citterio D, Suzuki K. Bright, color-tunable fluorescent dyes in the visible-near-infrared region. J Am Chem Soc 2008;130:1550.
 - (b) Umezawa K, Matsui A, Nakamura Y, Citterio D, Suzuki K. Bright, color-tunable fluorescent dyes in the Vis/NIR region: establishment of new "tailor-made" multicolor fluorophores based on borondipyrromethene. Chem Eur J 2009;15:1096.
 - (c) Awuah SG, Polreis J, Biradar V, You Y. Singlet oxygen generation by novel NIR BODIPY dyes. Org Lett 2011;13:3884.
 - (d) Wang YW, Descalzo AB, Shen Z, You XZ, Rurack K. Dihydronaphthalene-fused boron-dipyrromethene (BODIPY) dyes: insight into the electronic and conformational tuning modes of BODIPY fluorophores. Chem Eur J 2010;16:2887.
 - (e) Kowada T, Yamaguchi S, Ohe K. Highly fluorescent BODIPY dyes modulated with spirofluorene moieties. Org Lett 2010;12:296.
 - (f) Heyer E, Retailleau P, Ziessel R. α-Fused dithienyl BODIPYs synthesized by oxidative ring closure. Org Lett 2014;16:2330.
 - (g) Wu Y, Cheng C, Jiao L, Yu C, Wang S, Hao E, et al. β -Thiophene-fused BF₂-azadipyrromethenes as near-infrared dyes. Org Lett 2014;16:748.
 - (h) Goze C, Ulrich G, Ziessel RTetrahedral boron chemistry for the preparation of highly efficient "cascatelle" devices. J Org Chem 2007;72:313.
 - (i) Davies LH, Stewart B, Harrington RW, Clegg W, Higham LJ. Air-stable, highly fluorescent primary phosphanes. Angew Chem Int Ed 2012;51:4921.
 - (j) Le Guennic B, Maury O, Jacquemin D. Aza-boron-dipyrromethene dyes: TD-DFT benchmarks, spectral analysis and design of original near-IR structures. Phys Chem Chem Phys 2012;14:157.
 - (k) Zhao W, Carreira EM. Conformationally restricted aza-bodipy: a highly fluorescent, stable, near-infrared-absorbing dye. Angew Chem Int Ed 2005;44:1677.
 - (l) Zhao W, Carreira EM. Conformationally restricted aza-BODIPY: highly fluorescent, stable near-infrared absorbing dyes. Chem Eur J 2006;12:7254.
 - (m) Huang L, Cui X, Therrien B, Zhao J. Energy-funneling-based broadband visible-light-absorbing bodipy- C_{60} triads and tetrads as dual functional heavy-atom-free organic triplet photosensitizers for photocatalytic organic reactions. Chem Eur J 2013;19:17472.

- [6] Killoran J, Allen L, Gallagher JF, Gallagher WM, O'Shea DF. Synthesis of BF₂ chelates of tetraarylazadipyrromethenes and evidence for their photodynamic therapeutic behaviour. Chem Commun 2002;1862.
- [7] (a) Lu H, Mack J, Yang Y, Shen Z. Structural modification strategies for the rational design of red/NIR region BODIPYs. Chem Soc Rev 2014;43:4778.

(b) Bellier Q, Pégaz S, Aronica C, Le Guennic B, Andraud C, Maury O. Near-Infrared Nitrofluorene Substitued Aza-Boron-dipyrromethenes Dyes. Org Lett 2011;13:22.

- [8] McDonnell SO, O'Shea DF. Near-infrared sensing properties of dimethlyamino-substituted BF₂-azadipyrromethenes. Org Lett 2006;8:3493.
- [9] Jiao L, Wu Y, Wang S, Hu X, Hao E, Vicente MG, et al. Accessing near-infrared-absorbing BF₂-azadipyrromethenes via a push-pull effect. J Org Chem 2014;79:1830.
- [10] Valero G, Companyó X, Rios R. Enantioselective organocatalytic synthesis of fluorinated molecules. Chem Eur J 2011;17:2018.
- [11] (a) Jiang XD, Kakuda K, Matsukawa S, Yamamichi H, Kojima S, Yamamoto Y. Synthesis and application of a bidentate ligand based on decafluoro-3-phenyl-3-pentanol: steric effect of pentafluoroethyl groups on the stereomutation of O-equatorial C-apical spirophosphoranes. Chem Asian J 2007;2:314.

(b) Jiang XD, Matsukawa S, Yamamichi H, Yamamoto Y. First isolation and kinetic study of hypervalent 10-As-5 organoarsenic compounds with a C-apical, O-equatorial configuration. Inorg Chem 2007;46:5480.

(c) Jiang XD, Matsukawa S, Yamamoto Y. Synthesis, structure and isomerization of arylphosphoranes with anti-apicophilic bonding modes using a novel bidentate ligand with two C_2F_5 groups. Dalton Trans 2008;28:3678.

(d) Jiang XD, Matsukawa S, Yamamichi H, Kakuda K, Kojima S, Yamamoto Y. Stereomutation and Experimental Determination of the Relative Stability of Diastereomeric O-Equatorial Anti-Apicophilic Spirophosphoranes. Eur J Org Chem 2008;1392.

(e) Jiang XD, Matsukawa S, Fukuzaki Y, Yamamoto Y. Formation of epoxides from pentacoordinated organoarsenic compounds with a b-hydroxyethyl group. New J Chem 2010;34:1623.

(f) Jiang XD, Matsukawa S, Kakuda K, Fukuzaki Y, Kojima S, Yamamoto Y, et al. Efficient synthesis of tetradecafluoro-4-phenylheptan-4-ol by a Cannizzaro-type reaction and application of the alcohol as a bulky Martin ligand variant for a new anti-apicophilic phosphorane. Dalton Trans 2010;39:9823.

(g) Jiang XD, Matsukawa S, Kojima S, Yamamoto Y. Synthesis and characterization of antiapicophilic arsoranes and related compounds. Inorg Chem 2012;51:10996.

[12] (a) Jiang XD, Zhang J, Furuyama T, Zhao W. Development of mono- and di-AcO substituted BODIPYs on the boron center. Org Lett 2012;14:248.

(b) Jiang XD, Zhang H, Zhang Y, Zhao W. Development of non-symmetric thiophene-fused BODIPYs. Tetrahedron 2012;68:9795.

(c) Jiang XD, Zhang J, Shao X, Zhao W. A selective fluorescent turn-on NIR probe for cysteine. Org Biomol Chem 2012;10:1966.

(d) Kang R, Shao X, Peng F, Zhang Y, Sun GT, Jiang XD, et al. A highly selective turn-on fluorescent chemosensor for Al^{3+} imaging in living cells via through-bond energy Transfer. RSC Adv 2013;3:21033.

(e) Jiang XD, Xi D, Sun C, Guan J, He M, Xiao LJ. Synthesis of a pyrene-fused aza-BODIPY as a near-infrared dye having the absorption maximum at 746 nm. Tetrahedron Lett **2015**;56:4868.

(f) Jiang XD, Zhao J, Xi D, Yu H, Guan J, Xiao LJ, et al. A new water-soluble phosphorus-dipyrromethene and phosphorus-azadipyrromethene dye: PODIPY/aza-PODIPY. Chem Eur J 2015;21:6079.

(g) Jiang XD, Li S, Guan J, Fang T, Liu X, Xiao LJ. Recent advances of the near-infrared fluorescent aza-BODIPY dyes. Curr Org Chem 2016;20:1736.

(h) Jiang XD, Guan J, Li Q, Sun C. New near-infrared fluorescent aza-BODIPY dyes with 1-methyl-1H-pyrrolyl substituents at 3,5-positions. Asian J Org Chem 2016;5:1063.

- [13] Gorman A, Killoran J, O'Shea C, Kenna T, Gallagher WM, O'Shea DF. In Vitro Demonstration of the Heavy-Atom Effect for Photodynamic Therapy. J Am Chem Soc 2004;126:10619.
- [14] Frisch MJ, Trucks GW, Schlegel HB, Scuseria GE, Robb MA, Cheeseman JR, et al. Gaussian 09W, revision A.1; Gaussian Inc.: Wallingford, CT, 2009.
- [15] (a) Jacquemin D, Planchat A, Adamo C, Mennucci B. TD-DFT Assessment of Functionals for Optical 0-0 Transitions in Solvated Dyes. J Chem Theory Comput 2012;8:2359.

(b) Zhao Y, Truhlar DG. The M06 suite of density functionals for main group thermochemistry, thermochemical kinetics, noncovalent interactions, excited states, and transition elements: two new functionals and systematic testing of four M06-class functionals and 12 other functionals. Theor Chem Acc 2008;120:215.

(c) Li R, Zheng J, Truhlar DG. Density functional approximations for charge transfer excitations with intermediate spatial overlap. Phys Chem Chem Phys 2010;12:12697.

(d) Isegawa M, Peverati R, Truhlar DG. Performance of recent and high-performance approximate density functionals for time-dependent density functional theory calculations of valence and Rydberg electronic transition energies. J Chem Phys 2012;137:244104.

(e) Leang SS, Zahariev F, Gordon MS. Benchmarking the performance of time-dependent density functional methods. J Chem Phys 2012;136:104101.

(f) Charaf-Eddin A, Planchat A, Mennucci B, Adamo C, Jacquemin D. Choosing a Functional for Computing Absorption and Fluorescence Band Shapes with TD-DFT. J Chem Theory Comput 2013;9:2749.

[16] Cossi M, Barone V. Time-dependent density functional theory for molecules in liquid solutions. J Chem Phys 2001;115:4708.

- [17] Improta R, Barone V, Scalmani G, Frisch MJ. A state-specific polarizable continuum model time dependent density functional theory method for excited state calculations in solution. J Chem Phys 2006;125:054103.
- [18] (a) Sanderson RT. Polar Covalence, New York: Aeademic Press, 1983, 37.
 - (b) Bratseh SG. A group electronegativity method with Pauling units. J Chem Educ 1985;62:101.
- [19] (a) Jiang XD, Gao R, Yue Y, Sun GT, Zhao W. A NIR BODIPY dye bearing 3,4,4a-trihydroxanthene moieties. Org Biomol Chem 2012;10:6861.
 - (b) Jiang XD, Xi D, Zhao J, Yu H, Sun GT, Xiao LJ. A styryl-containing aza-BODIPY as a near-infrared dye. RSC Adv 2014;4:60970.
 - (c) Jiang XD, Zhao J, Li Q, Sun CL, Guan J, Xiao LJ, et al. Synthesis of NIR fluorescent thienyl-containing aza-BODIPY and its application for detection of Hg²⁺: Electron transfer by bonding with Hg²⁺. Dyes Pigm 2016;125:136.
- [20] Lippert AR, New EJ, Chang CJ. Reaction-based fluorescent probes for selective imaging of hydrogen sulfide in living cells. J Am Chem Soc 2011;133:10078.
- [21] (a) Thivierge C, Han J, Jenkins RM, Burgess K. Fluorescent Proton Sensors Based on Energy Transfer. J Org Chem 2011;76:5219.

(b) Czarnik AW. Chemical Communication in Water Using Fluorescent Chemosensors. Acc Chem Res 1994;27:302.

(c) Jager WF, Hammink TS, van den Berg O, Grozema FC. Highly Sensitive Water-Soluble Fluorescent pH Sensors Based on the 7-Amino-1-methylquinolinium Chromophore. J Org Chem 2010;75:2169.

- [22] Rurack K, Kollmannsberger M, Daub J. Molecular Switching in the Near Infrared (NIR) with a Functionalized Boron–Dipyrromethene Dye. Angew Chem Int Ed 2001;40:385.
- [23] Chibani S, Laurent AD, Le Guennic B, Jacquemin D. Improving the Accuracy of Excited-State Simulations of BODIPY and Aza-BODIPY Dyes with a Joint SOS-CIS(D) and TD-DFT Approach. J Chem Theory Comput 2014;10:4574.
- [24]Le Guennic B, Jacquemin D. Taking up the cyanine challenge with quantum tools. Acc Chem Res 2015;48:530.
- [25](a) Le Bahers T, Adamo C, Ciofini I. A Qualitative Index of Spatial Extent in Charge-Transfer Excitations. J Chem Theory Comput 2011;7:2498.

(b) Jacquemin D, Le Bahers T, Adamo C, Ciofini I. What is the "best" atomic charge model to describe through-space charge-transfer excitations? Phys Chem Chem Phys 2012;14:5383.

Fig. 1. (a) BODIPY vs. aza-BODIPY. (b) Structures of some previously reported aza-BODIPYs [6,8,9].

Scheme 1 Synthesis of fluorine-containing pyrroles 1 and 2.

Scheme 2 Synthesis of fluorine-containing aza-BODIPYs 3-6.

Fig. 2. ORTEP diagram of **4** showing the thermal ellipsoids at the 30% probability level. All hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): B1-F1, 1.349(4); B1-N1, 1.518(5); N1-C8, 1.344(5); N1-C11, 1.365(5); N2-C11, 1.301(5); F2-C15, 1.278(9); C(11*)-N(2)-C(11)-C(10), 179.9(5).

Scheme 3 Synthesis of aza-BODIPYs 9 and 10.

Table 1 Photophysical properties of aza-BODIPYs 3-10 in CHCl₃ at 298 K.

Fig. 3. (a) Normalized absorption and (b) fluorescence spectra of aza-BODIPYs **3** (black curve), **4** (blue curve), **5** (red curve) and **6** (green curve) in CHCl₃ at 298 K. Photoimages of **3-6** under normal room illumination in CHCl₃ at 298 K.

Fig. 4. (a) Normalized absorption and (b) fluorescence spectra of aza-BODIPYs **9** (red curve) and **10** (black curve) in CHCl₃ at 298 K.

Fig. 5. Absorption (a) and fluorescence (b) spectra (pH 7, 6, 5, 4, 3, 2, 1.8, 1.6, 1.4, 1.2, 1 and 1 M, 2 M, 4 M, 6 M of HCl) of 2 μ M dye **10** in DMSO/H₂O (2:1, v/v) as a function of pH. $\lambda_{ex} = 700$ nm.

Table 2 Computed λ_{abs} and λ_{em} (in nm), AFCP energy (E^{AFCP}, in nm), charge transfer distances (d^{CT}, in Å), and transferred charges (q^{CT}, in e) of aza-BODIPYs **3**, **4**, **5**, **6**, **8**, **9** and **10** at the cLR-PCM(CHCl₃)-M06-2X/6-311+G(2d,p)/SOS-CIS(D).

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Fig. 6. Density difference plots for (from left to right and top to bottom) aza-BODIPYs 3, 4, 5, 6, 9 and 10. The blue (red) zones indicate density decrease (increase) upon transition.



Fig. 1 (a) BODIPY vs. aza-BODIPY. (b) Structures of some previously reported aza-BODIPYs [6,8,9].



Scheme 1 Synthesis of fluorine-containing pyrroles 1 and 2.



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Scheme 3 Synthesis of aza-BODIPYs 9 and 10.

Dye	$\lambda_{\rm abs}/\lambda_{\rm em}$	Stokes'	FWHM	\mathcal{E} [M ⁻¹	$arPsi_{f}$
2	[nm]	shift [cm ⁻¹]	[nm]	cm ⁻¹]	5
3	650/674	25	49	80000	0.34
4	688/715	27	55	86000	0.36
5	650/672	25	49	79000	0.34
6	688/715	27	55	85000	0.36
7 [13]	650/672	25	49	79000	0.34
8 [13]	688/715	27	55	85000	0.36
9	710/754	44	86	67000	0.26
10	699/749	50	68	52000	0.03

Table 1 Photophysical properties of aza-BODIPYs 3-10 in CHCl₃ at 298 K.



Fig. 3. (a) Normalized absorption and (b) fluorescence spectra of aza-BODIPYs **3** (black curve), **4** (blue curve), **5** (red curve) and **6** (green curve) in CHCl₃ at 298 K. Photoimages of **3-6** under normal room illumination in CHCl₃ at 298 K.





Fig. 4. (a) Normalized absorption and (b) fluorescence spectra of aza-BODIPYs 9 (red curve) and 10 (black curve) in $CHCl_3$ at 298 K.





Fig. 5. Absorption (a) and fluorescence (b) spectra (pH 7, 6, 5, 4, 3, 2, 1.8, 1.6, 1.4, 1.2, 1 and 1 M, 2 M, 4 M, 6 M of HCl) of 3 μ M dye **10** in DMSO/H₂O (2:1, v/v) as a function of pH. λ_{ex} = 700 nm.

Dye	λ_{abs}	λ_{em}	EAFCP	d^{CT}	q^{CT}
	[nm]	[nm]	[nm]	[Å]	[e]
3	664	717	706	0.56	0.34
4	704	770	755	1.44	0.39
5	664	717	710	0.61	0.34
6	703	769	752	1.44	0.39
8	702	768	752	1.47	0.39
9	714	783	769	1.11	0.38
10	716	798	770	0.56	0.39

Table 2 Computed λ_{abs} and λ_{em} (in nm), AFCP energy (E^{AFCP}, in nm), charge transfer distances (d^{CT}, in Å), and transferred charges (q^{CT}, in e) of aza-BODIPYs **3**, **4**, **5**, **6**, **8**, **9** and **10** at the cLR-PCM(CHCl₃)-M06-2X/6-311+G(2d,p)/SOS-CIS(D).



Fig. 6. Density difference plots for (from left to right and top to bottom) aza-BODIPYs 3, 4, 5, 6, 9 and 10. The blue (red) zones indicate density decrease (increase) upon transition.

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Synthesis, structure and photophysical properties of NIR aza-BODIPYs with $-F/-N_3/-NH_2$ groups at 1,7-positions

Xin-Dong Jiang, ^{a,b}* Jian Guan, ^a Jiuli zhao, ^a Boris Le Guennic, ^{c,*} Denis Jacquemin, ^d Zhigang Zhang^a Shangdong Chen^a and Linjiu Xiao^a

NMR
HRMS
X-ray single crystal diffraction data of 4
Ground state geometries in gas phase



¹H NMR of 3-(4-fluorophenyl)-2*H*-azirine









¹³C NMR of aza-BODIPY 3



¹H NMR of aza-BODIPY 4



¹³C NMR of aza-BODIPY 4



¹H NMR of aza-BODIPY 5



¹³C NMR of aza-BODIPY 5



¹H NMR of aza-BODIPY 6



¹³C NMR of aza-BODIPY 6



¹H NMR of aza-BODIPY 9



¹H NMR of aza-BODIPY 10

2. HRMS

使用仪器:

Thermo Scientific LTQ Orbitrap XL

离**子源:**ESI

检测结果:

1. HRMS (ESI) m/z calcd for $C_{16}H_{13}FN^+$ (M+H)⁺ 238.10265, found 238.10268.



2. HRMS (ESI) m/z calcd for C₁₇H₁₅FNO⁺ (M+H)⁺ 268.11322, found 268.11322.



HRMS for 2

	Mass S	pectrum Mole	ecular Fo	rmula Repo	ort		
Analysis Info	D:\Data\20150115CEY	ANG\2.d			0.000		
Analysis Name				Acquisition Date	1/15/201	5 11:13:26 A	MA
Nethod	tune_wide_pos.m			Operator	micrOT	OF-Q	
Sample Name	2			Instrument / Ser#	Bruker C	ustomer 125	
Comment							
Acquisition Pa	rameter	ez kinazan		2.2.550000050		2000.000	
Source Type	ESI	Ion Polarity	Positive	Set Nebulize	r	0.3 Bar	
ocus	Active	Set Capillary	4500 V	Set Dry Hea	ter	180 °C	
ican Begin	50 m/z 3000 m/z	Set End Plate Offset	-500 V	Set Dry Gas	alura	4.0 I/min	
scan Enu	3000 m/2	Set Collision Cell RF	600.0 Vpp	Set Divert Vi	aive	Source	
Senerate Mole	cular Formula Paramete	ər					
ormula, min.	C32H2UB1F4N3Na						
feasured m/z	555 159	Toloranco	5 0000	Charge	4		
check Valence	000.100	Minimum	0	Maximum	ò		
lirogen Rule	no	Electron Confi	guration both				
ilter H/C Ratio	no	Minimum	0	Maximum	3		
stimate Carbon	yes						
x10 ⁵			556 1583			+IVIS, U.8	min #4¢
0.6-			000.1000				
0.4-				572 1291			
1							
0.2-		534.1727	1 × 1				
0.000			- 1 I I -	1.1			
							1.
0.0		┍┱╌┍┸┥╧┟┍╌┲╌┲╌┲				and the stand of the	- Herrison
0.0 500	510 520	530 540	550 56	570	580	590	m/z
0.0	510 520 Sum Formula Sigma	530 540 m/z Err [ppm]	550 56 Mean Err (ppm	0 570	580 N Rule	590 e	m/2

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HRMS for 3



3. HRMS (ESI) m/z calcd for $C_{34}H_{25}BF_4N_3O_2^+$ (M+H)⁺ 594.19705, found 594.19678.

4. HRMS (ESI) m/z calcd for $C_{32}H_{22}BF_3N_3^+$ (M+H)⁺ 516.18534, found 516.18463.



HRMS for 5

	made op		oundin i o	iniula Nepu	n c	
Analysis Info Analysis Name Method Sample Name Comment	D:\Data\20150115CEYA tune_wide_pos.m 3	NG\3.d		Acquisition Date Operator Instrument / Ser#	1/15/20 micrOT Bruker (15 11:16:31 AM "OF-Q Customer 125
Acquisition Par Source Type Focus Scan Begin Scan End	ameter ESI Active 50 m/z 3000 m/z	Ion Polarity Set Capillary Set End Plate Offset Set Collision Cell RF	Positive 4500 V -500 V 600.0 Vpp	Set Nebuliz Set Dry Hea Set Dry Gas Set Divert V	er ter alve	0.3 Bar 180 °C 4.0 I/min Source
Generate Molect Formula, min. Formula, max. Measured m/z Check Valence Nirogen Rule Filter H/C Ratio Estimate Carbon	cular Formula Parameter C34H25B1F3N3O2Na 598.189 no no no yes	Tolerance Minimum Electron Config Minimum	5 ppm 0 uration both 0	Charge Maximun Maximun	1 0 1 3	
Intens. x10 ⁴ 1.5						+MS, 0.3min #17
0.0 560 C 34 H 25	570 58 Sum Formula Sign B 1 F 3 N 3 Na 1 O 2 0.0	<mark>1</mark>	600 m] Mean Err .81	610 [ppm] Err [mDa] 0.47 -0.49	rdb N 22.50	620 m/2 Rule e [–] ok even
Bruker Daltonics	s DataAnalysis 3.4	printed:	1/15/2015 6	5:55:40 PM		Page 1 of 1



5. HRMS (ESI) m/z calcd for $C_{34}H_{29}BF_2N_5O_2^+$ (M+H)⁺ 588.23769, found 588.23730.

6. HRMS (ESI) m/z calcd for C₃₄H₂₇BF₃N₄O₂⁺ (M+H)⁺ 591.21737, found 591.21777.



HRMS for 10

3. X-ray single crystal diffraction data of 4

Crystals suitable for the X-ray structural determination were mounted on a Mac Science DIP2030 imaging plate diffractometer and irradiated with graphite monochromated Mo-K α radiation ($\lambda = 0.71073$ Å) for the data collection. The unit cell parameters were determined by separately autoindexing several images in each data set using the DENZO program (MAC Science). For each data set, the rotation images were collected in 3 degree increments with a total rotation of 180 deg about the ϕ axis. The data were processed using SCALEPACK. The structures were solved by a direct method with the SHELX-97 program. Refinement on F^2 was carried out using the full-matrix least-squares by the SHELX-97 program. All non-hydrogen atoms were refined using the anisotropic thermal parameters. The hydrogen atoms were included in the refinement along with the isotropic thermal parameters (Table S1-S5).



shelx

Table S1. Crystal data and structure refinement. Identification code Empirical formula Formula weight Temperature Wavelength Crystal system Space group Unit cell dimensions

Volume Ζ Density (calculated) Absorption coefficient F(000) Crystal size Theta range for data collection Index ranges Reflections collected Independent reflections Completeness to theta = 28.38° Max. and min. transmission Refinement method Data / restraints / parameters Goodness-of-fit on F² Final R indices [I>2sigma(I)] R indices (all data) Extinction coefficient Largest diff. peak and hole

C34 H24 B F4 N3 O2 593.37 293(2) K 0.71073 Å ? Ia-3d a = 16.1853(2) Å $\alpha = 90^{\circ}$ β= 90° b = 16.1853(2) Å c = 19.9274(6) Å $\gamma = 90^{\circ}$ 5220.26(18) Å3 48 9.060 Mg/m³ 0.683 mm⁻¹ 14688 0.40 x 0.30 x 0.20 mm³ 3.24 to 28.38°. -21<=h<=21, -21<=k<=21, -26<=l<=26 23013 3276 [R(int) = 0.0867] 99.8 % 0.8756 and 0.7719 Full-matrix least-squares on F² 3276 / 0 / 202 2.181 R1 = 0.1437, wR2 = 0.3623 R1 = 0.1832, wR2 = 0.4016 0.0002(6) 1.077 and -0.724 e.Å-3

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	Х	У	Z	U(eq)
F(1)	4356(2)	2252(2)	52(1)	68(1)
N(1)	4724(2)	3202(2)	885(2)	56(1)
N(2)	5000	2500	1895(2)	57(1)
C(11)	4754(3)	3150(3)	1568(2)	57(1)
C(8)	4405(3)	3946(3)	732(2)	58(1)
C(5)	4206(3)	4249(3)	81(2)	59(1)
C(10)	4471(3)	3893(3)	1848(2)	59(1)
O(1)	3564(2)	5205(2)	-1736(2)	89(1)
C(9)	4269(3)	4355(3)	1333(2)	65(1)
C(12)	4440(3)	4104(3)	2551(2)	60(1)
C(2)	3755(3)	4932(3)	-1130(2)	69(1)
C(3)	4209(3)	4242(3)	-1115(2)	72(1)
C(4)	4431(3)	3912(3)	-523(2)	71(1)
C(6)	3730(3)	4966(3)	42(2)	79(1)
C(15)	4374(4)	4560(4)	3832(2)	87(2)
C(13)	4194(3)	3561(3)	3029(3)	79(1)
C(17)	4604(3)	4870(3)	2739(3)	85(2)
C(7)	3504(4)	5296(3)	-541(2)	81(2)
B(1)	5000	2500	432(3)	55(2)
C(16)	4576(4)	5107(3)	3395(3)	90(2)
C(14)	4152(4)	3771(4)	3686(2)	88(2)
F(2)	4452(7)	4791(5)	4443(4)	270(4)
C(1)	3093(6)	5936(5)	-1790(4)	142(3)

Table S2. Atomic coordinates (Å x 10⁴) and equivalent isotropic displacement parameters (Å²x 10³). U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

R CR

N(1)-C(8)1.344(5)N(1)-C(11)1.365(5)N(1)-B(1)1.518(5)N(2)-C(11)#11.301(5)C(2)-C(1)#11.301(5)C(1)-C(10)1.403(6)C(8)-C(9)1.387(6)C(5)-C(4)1.370(6)C(5)-C(6)1.396(6)C(10)-C(12)1.442(6)O(1)-C(12)1.442(6)O(1)-C(12)1.442(6)O(1)-C(12)1.442(6)O(1)-C(12)1.322(7)C(12)-C(17)1.322(7)C(12)-C(13)1.356(7)C(2)-C(3)1.338(7)C(2)-C(3)1.338(7)C(2)-C(7)1.330(6)C(6)-C(7)1.330(6)C(15)-C(16)1.285(8)C(15)-C(16)1.285(8)C(13)-C(14)1.357(7)C(17)-C(16)1.335(7)C(17)-C(16)1.335(7)C(17)-C(16)1.335(7)C(17)-C(16)1.355(7)C(17)-C(16)1.355(7)C(17)-C(16)1.355(7)C(17)-C(16)1.355(7)C(17)-C(16)1.355(7)C(17)-C(16)1.355(7)C(17)-C(16)1.35(3)C(11)-N(1)-B(1)122.4(3)C(11)-N(1)-B(1)122.4(3)C(11)-N(1)-B(1)122.4(3)C(11)-N(1)-B(1)124.4(3)N(1)-C(8)-C(9)107.1(4)N(1)-C(8)-C(5)125.9(4)C(4)-C(5)-C(6)115.4(4)C(4)-C(5)-C(8)127.1(4)	F(1)-B(1)	1.349(4)	
N(1)-C(11)1.365(5)N(1)-B(1)1.518(5)N(2)-C(11)#11.301(5)C(2)-C(1)#11.301(6)C(1)-C(10)1.403(6)C(8)-C(9)1.387(6)C(8)-C(5)1.425(6)C(5)-C(4)1.370(6)C(5)-C(6)1.396(6)C(10)-C(12)1.442(6)O(1)-C(2)1.322(5)O(1)-C(2)1.322(7)C(12)-C(13)1.356(7)C(2)-C(7)1.376(7)C(2)-C(7)1.376(7)C(2)-C(7)1.330(6)C(15)-F(2)1.278(9)C(15)-C(16)1.285(8)C(15)-C(16)1.285(8)C(15)-C(14)1.357(8)C(15)-C(14)1.355(7)C(17)-C(16)1.363(7)B(1)-F(1)#11.349(4)B(1)-N(1)#11.518(5)C(8)-N(1)-C(11)107.1(3)C(8)-N(1)-C(11)107.1(3)C(8)-N(1)-C(11)107.1(3)C(8)-N(1)-C(11)105.(3)C(11)-N(1)-B(1)124.1(4)N(1)-C(8)-C(5)125.9(4)C(1)-N(1)-C(10)199.5(4)N(1)-C(8)-C(5)125.9(4)C(9)-C(8)-C(5)125.9(4)C(9)-C(8)-C(6)115.4(4)C(4)-C(5)-C(6)115.4(4)C(4)-C(5)-C(8)127.1(4)	N(1)-C(8)	1.344(5)	
N(1)-B(1)1.518(5)N(2)-C(11)#11.301(5)C(1)-C(10)1.403(6)C(8)-C(9)1.387(6)C(8)-C(9)1.387(6)C(5)-C(4)1.370(6)C(5)-C(4)1.370(6)C(10)-C(12)1.442(6)O(1)-C(2)1.322(5)O(1)-C(12)1.442(6)O(1)-C(12)1.442(6)O(1)-C(2)1.322(7)C(12)-C(17)1.322(7)C(2)-C(13)1.356(7)C(2)-C(7)1.376(7)C(2)-C(7)1.330(6)C(15)-F(2)1.278(9)C(15)-F(2)1.278(9)C(15)-C(14)1.355(7)C(12)-C(14)1.355(7)C(15)-C(14)1.355(7)C(17)-C(16)1.285(8)C(13)-C(14)1.355(7)C(17)-C(16)1.363(7)B(1)-F(1)#11.349(4)B(1)-N(1)#11.518(5)C(8)-N(1)-C(11)107.1(3)C(8)-N(1)-C(11)107.1(3)C(11)-N(2)-C(11)#1119.8(5)N(2)-C(11)-N(1)124.1(4)N(2)-C(11)-N(1)124.1(4)N(1)-C(8)-C(9)107.1(4)N(1)-C(8)-C(5)126.9(4)C(1)-N(1)-C(10)109.5(4)N(1)-C(8)-C(5)126.9(4)C(4)-C(5)-C(6)115.4(4)C(4)-C(5)-C(6)115.4(4)C(4)-C(5)-C(6)115.4(4)C(4)-C(5)-C(8)127.1(4)	N(1)-C(11)	1.365(5)	
N(2)-C(11)1.301(5)N(2)-C(11)#11.301(5)C(11)-C(10)1.403(6)C(8)-C(3)1.387(6)C(8)-C(3)1.425(6)C(5)-C(4)1.370(6)C(5)-C(6)1.396(6)C(10)-C(9)1.311(6)C(10)-C(12)1.442(6)O(1)-C(1)1.411(8)C(12)-C(17)1.322(7)C(12)-C(13)1.356(7)C(2)-C(13)1.356(7)C(2)-C(13)1.338(7)C(2)-C(7)1.376(7)C(3)-C(4)1.343(6)C(15)-F(2)1.278(9)C(15)-F(2)1.278(9)C(15)-C(14)1.355(7)C(17)-C(16)1.363(7)B(1)-F(1)#11.349(4)B(1)-N(1)#11.518(5)C(8)-N(1)-C(11)107.1(3)C(8)-N(1)-C(11)107.1(3)C(8)-N(1)-C(11)122.4(3)C(11)-N(1)-B(1)123.6(5)N(2)-C(11)#1119.8(5)N(2)-C(11)#1119.8(5)N(2)-C(11)-C(10)126.4(4)N(1)-C(8)-C(5)126.9(4)C(9)-C(5)125.9(4)C(4)-C(5)-C(6)115.4(4)C(4)-C(5)-C(6)115.4(4)C(4)-C(5)-C(8)127.1(4)	N(1)-B(1)	1.518(5)	
N(2)-C(11)#11.301(5)C(11)-C(10)1.403(6)C(8)-C(9)1.387(6)C(8)-C(5)1.425(6)C(5)-C(6)1.396(6)C(10)-C(9)1.311(6)C(10)-C(12)1.442(6)O(1)-C(2)1.322(5)O(1)-C(12)1.441(8)C(12)-C(17)1.322(7)C(12)-C(13)1.356(7)C(2)-C(3)1.338(7)C(2)-C(3)1.338(7)C(2)-C(7)1.376(7)C(3)-C(4)1.343(6)C(15)-F(2)1.278(9)C(15)-F(14)1.355(7)C(15)-C(14)1.355(7)C(13)-C(14)1.355(7)C(17)-C(16)1.333(7)B(1)-F(1)#11.349(4)B(1)-N(1)#11.518(5)C(8)-N(1)-C(11)107.1(3)C(8)-N(1)-C(11)107.1(3)C(8)-N(1)-C(11)122.4(3)C(11)-N(1)-B(1)122.4(3)C(11)-N(1)-B(1)126.4(4)N(1)-C(11)-C(10)126.4(4)N(1)-C(11)-C(10)126.4(4)N(1)-C(1)-C(10)126.4(4)N(1)-C(1)-C(10)126.4(4)N(1)-C(5)-C(5)126.9(4)C(9)-C(5)125.9(4)C(4)-C(5)-C(6)115.4(4)C(4)-C(5)-C(6)115.4(4)C(4)-C(5)-C(8)127.1(4)	N(2)-C(11)	1.301(5)	
C(11)-C(10)1.403(6)C(8)-C(9)1.387(6)C(8)-C(5)1.425(6)C(5)-C(4)1.370(6)C(5)-C(6)1.396(6)C(10)-C(9)1.311(6)C(10)-C(12)1.442(6)O(1)-C(2)1.322(5)O(1)-C(1)1.411(8)C(12)-C(17)1.322(7)C(12)-C(13)1.356(7)C(2)-C(7)1.376(7)C(3)-C(4)1.343(6)C(6)-C(7)1.330(6)C(15)-F(2)1.278(9)C(15)-C(16)1.285(8)C(15)-C(14)1.357(8)C(13)-C(14)1.355(7)C(17)-C(16)1.343(4)B(1)-F(1)#11.349(4)B(1)-F(1)#11.349(4)B(1)-F(1)#11.349(4)B(1)-F(1)#11.349(4)B(1)-F(1)#11.349(4)N(1)-C(11)107.1(3)C(8)-N(1)-C(11)107.1(3)C(8)-N(1)-C(11)122.4(3)C(11)-N(1)-B(1)122.4(3)C(11)-N(1)-B(1)124.1(4)N(2)-C(11)-C(10)126.4(4)N(1)-C(10)109.5(4)N(1)-C(10)126.4(4)N(1)-C(10)126.4(4)N(1)-C(10)126.4(4)N(1)-C(10)126.4(4)N(1)-C(10)126.4(4)N(1)-C(10)126.4(4)N(1)-C(10)126.4(4)N(1)-C(10)126.4(4)N(1)-C(10)126.4(4)N(1)-C(10)126.4(4)N(1)-C(10)126.4(4)N(1)-C(10)126.4(4)N(1)-C(10)126.4(4)N(1)-C(10)	N(2)-C(11)#1	1.301(5)	
C(8)-C(9)1.387(6)C(8)-C(5)1.425(6)C(5)-C(4)1.370(6)C(5)-C(6)1.396(6)C(10)-C(9)1.311(6)C(10)-C(12)1.442(6)O(1)-C(2)1.322(5)O(1)-C(1)1.411(8)C(12)-C(17)1.322(7)C(12)-C(13)1.356(7)C(2)-C(7)1.338(7)C(2)-C(7)1.338(7)C(2)-C(7)1.330(6)C(6)-C(7)1.330(6)C(15)-F(2)1.278(9)C(15)-C(16)1.285(8)C(15)-C(16)1.285(8)C(15)-C(14)1.355(7)C(17)-C(16)4.363(7)B(1)-F(1)#11.349(4)B(1)-N(1)#11.518(5)C(8)-N(1)-C(11)107.1(3)C(8)-N(1)-C(11)107.1(3)C(8)-N(1)-C(11)119.8(5)N(2)-C(11)-R(1)122.4(3)C(11)-N(1)-B(1)122.4(3)C(11)-N(1)-B(1)124.1(4)N(2)-C(11)-C(10)109.5(4)N(1)-C(11)-C(10)109.5(4)N(1)-C(11)-C(10)109.5(4)N(1)-C(8)-C(5)126.9(4)C(4)-C(5)-C(6)115.4(4)C(4)-C(5)-C(6)115.4(4)C(4)-C(5)-C(8)127.1(4)C(6)-C(5)-C(8)117.4(4)	C(11)-C(10)	1.403(6)	
C(8)-C(5)1.425(6) $C(5)-C(4)$ 1.370(6) $C(5)-C(6)$ 1.396(6) $C(10)-C(19)$ 1.311(6) $C(10)-C(12)$ 1.442(6) $O(1)-C(2)$ 1.3322(5) $O(1)-C(1)$ 1.411(8) $C(12)-C(17)$ 1.322(7) $C(12)-C(13)$ 1.356(7) $C(2)-C(3)$ 1.338(7) $C(2)-C(7)$ 1.376(7) $C(3)-C(4)$ 1.343(6) $C(6)-C(7)$ 1.330(6) $C(15)-F(2)$ 1.278(9) $C(15)-C(16)$ 1.285(8) $C(15)-C(14)$ 1.357(8) $C(15)-C(14)$ 1.357(8) $C(15)-C(14)$ 1.353(7) $C(17)-C(16)$ 1.363(7) $B(1)-F(1)#1$ 1.349(4) $B(1)-F(1)#1$ 1.349(4) $B(1)-N(1)-B(1)$ 107.1(3) $C(8)-N(1)-C(11)$ 107.1(3) $C(8)-N(1)-C(11)$ 107.1(3) $C(8)-N(1)-C(11)$ 107.1(3) $C(8)-N(1)-C(11)$ 107.1(3) $C(11)-N(1)-B(1)$ 122.4(3) $C(11)-N(1)-B(1)$ 122.4(3) $C(11)-N(1)-B(1)$ 124.1(4) $N(2)-C(11)-F(10)$ 126.4(4) $N(1)-C(10)$ 126.4(4) $N(1)-C(10)$ 126.4(4) $N(1)-C(1)-C(10)$ 126.4(4) $N(1)-C(2)-C(5)$ 126.9(4) $C(4)-C(5)$	C(8)-C(9)	1.387(6)	
C(5)-C(4)1.370(6) $C(5)-C(6)$ 1.396(6) $C(10)-C(2)$ 1.311(6) $C(10)-C(12)$ 1.442(6) $O(1)-C(1)$ 1.411(8) $C(12)-C(17)$ 1.322(7) $C(12)-C(17)$ 1.322(7) $C(2)-C(13)$ 1.356(7) $C(2)-C(13)$ 1.356(7) $C(2)-C(13)$ 1.376(7) $C(2)-C(7)$ 1.376(7) $C(3)-C(4)$ 1.343(6) $C(6)-C(7)$ 1.330(6) $C(15)-F(2)$ 1.278(9) $C(15)-C(16)$ 1.285(8) $C(15)-C(14)$ 1.355(7) $C(17)-C(16)$ 1.363(7) $B(1)-F(1)#1$ 1.349(4) $B(1)-F(1)#1$ 1.349(4) $B(1)-N(1)#1$ 1.518(5) $C(8)-N(1)-C(11)$ 107.1(3) $C(8)-N(1)-C(11)$ 107.1(3) $C(8)-N(1)-B(1)$ 122.4(3) $C(11)-N(2)-C(11)#1$ 119.8(5) $N(2)-C(11)-R(1)$ 124.1(4) $N(2)-C(11)-R(10)$ 126.4(4) $N(1)-C(8)-C(9)$ 107.1(4) $N(1)-C(8)-C(9)$ 107.1(4) $N(1)-C(8)-C(5)$ 126.9(4) $C(4)-C(5)-C(6)$ 115.4(4) $C(4)-C(5)-C(6)$ 115.4(4) $C(4)-C(5)-C(6)$ 117.4(4)	C(8)-C(5)	1.425(6)	
C(5)-C(6)1.396(6) $C(10)-C(9)$ 1.311(6) $C(10)-C(12)$ 1.442(6) $O(1)-C(2)$ 1.322(5) $O(1)-C(1)$ 1.411(8) $C(12)-C(17)$ 1.322(7) $C(12)-C(13)$ 1.356(7) $C(2)-C(3)$ 1.338(7) $C(2)-C(3)$ 1.338(7) $C(2)-C(7)$ 1.376(7) $C(3)-C(4)$ 1.343(6) $C(6)-C(7)$ 1.330(6) $C(15)-F(2)$ 1.278(9) $C(15)-C(16)$ 1.285(8) $C(15)-C(14)$ 1.357(8) $C(13)-C(14)$ 1.355(7) $C(17)-C(16)$ 1.363(7) $B(1)-F(1)#1$ 1.349(4) $B(1)-N(1)#1$ 1.518(5) $C(8)-N(1)-C(11)$ 107.1(3) $C(8)-N(1)-B(1)$ 122.4(3) $C(11)-N(1)-B(1)$ 124.1(4) $N(2)-C(11)-M(1)$ 124.1(4) $N(2)-C(11)-M(1)$ 126.4(4) $N(1)-C(8)-C(9)$ 107.1(4) $N(1)-C(8)-C(9)$ 107.1(4) $N(1)-C(8)-C(5)$ 126.9(4) $C(9)-C(8)-C(5)$ 125.9(4) $C(4)-C(5)-C(6)$ 115.4(4) $C(4)-C(5)-C(8)$ 127.1(4) $C(4)-C(5)-C(8)$ 127.1(4)	C(5)-C(4)	1.370(6)	
C(10)-C(9)1.311(6)C(10)-C(12)1.442(6)O(1)-C(2)1.322(5)O(1)-C(1)1.411(8)C(12)-C(17)1.322(7)C(12)-C(13)1.356(7)C(2)-C(3)1.338(7)C(2)-C(7)1.376(7)C(3)-C(4)1.343(6)C(6)-C(7)1.330(6)C(15)-F(2)1.278(9)C(15)-C(16)1.285(8)C(15)-C(14)1.357(8)C(13)-C(14)1.355(7)C(17)-C(16)1.363(7)B(1)-F(1)#11.349(4)B(1)-F(1)#11.518(5)C(8)-N(1)-C(11)107.1(3)C(8)-N(1)-B(1)122.4(3)C(11)-N(1)-B(1)122.4(3)C(11)-N(2)-C(11)#1119.8(5)N(2)-C(11)-R(1)126.4(4)N(1)-C(10)126.4(4)N(1)-C(10)109.5(4)N(1)-C(8)-C(9)107.1(4)N(1)-C(8)-C(5)125.9(4)C(4)-C(5)-C(6)115.4(4)C(4)-C(5)-C(6)115.4(4)C(4)-C(5)-C(6)117.4(4)	C(5)-C(6)	1.396(6)	
C(10)-C(12) $1.442(6)$ O(1)-C(2) $1.322(5)$ O(1)-C(1) $1.411(8)$ C(12)-C(17) $1.322(7)$ C(12)-C(13) $1.356(7)$ C(2)-C(3) $1.338(7)$ C(2)-C(7) $1.376(7)$ C(3)-C(4) $1.333(6)$ C(6)-C(7) $1.330(6)$ C(15)-F(2) $1.278(9)$ C(15)-C(16) $1.285(8)$ C(15)-C(14) $1.357(7)$ C(17)-C(16) $1.363(7)$ B(1)-F(1)#1 $1.349(4)$ B(1)-F(1)#1 $1.349(4)$ B(1)-N(1)-B(1) $107.1(3)$ C(8)-N(1)-C(11) $107.1(3)$ C(8)-N(1)-B(1) $130.5(3)$ C(11)-N(1)-B(1) $122.4(3)$ C(11)-N(1)-B(1) $122.4(3)$ C(11)-N(1)-B(1) $124.1(4)$ N(2)-C(11)-N(1) $124.1(4)$ N(2)-C(11)-N(1) $124.1(4)$ N(1)-C(8)-C(9) $107.1(4)$ N(1)-C(8)-C(5) $125.9(4)$ C(9)-C(8)-C(5) $125.9(4)$ C(4)-C(5)-C(6) $115.4(4)$ C(4)-C(5)-C(8) $127.1(4)$	C(10)-C(9)	1.311(6)	
O(1)-C(2) $1.322(5)$ $O(1)-C(1)$ $1.411(8)$ $C(12)-C(17)$ $1.322(7)$ $C(12)-C(13)$ $1.356(7)$ $C(2)-C(3)$ $1.338(7)$ $C(2)-C(7)$ $1.376(7)$ $C(3)-C(4)$ $1.343(6)$ $C(6)-C(7)$ $1.330(6)$ $C(15)-F(2)$ $1.278(9)$ $C(15)-C(16)$ $1.285(8)$ $C(15)-C(14)$ $1.357(8)$ $C(13)-C(14)$ $1.355(7)$ $C(17)-C(16)$ $1.363(7)$ $B(1)-F(1)#1$ $1.349(4)$ $B(1)-N(1)#1$ $1518(5)$ $C(8)-N(1)-C(11)$ $107.1(3)$ $C(8)-N(1)-C(11)$ $107.1(3)$ $C(8)-N(1)-C(11)$ $107.1(3)$ $C(8)-N(1)-C(11)$ $122.4(3)$ $C(11)-N(1)-B(1)$ $122.4(3)$ $C(11)-N(2)-C(11)#1$ $119.8(5)$ $N(2)-C(11)-N(1)$ $124.1(4)$ $N(2)-C(11)-N(1)$ $126.4(4)$ $N(1)-C(8)-C(9)$ $107.1(4)$ $N(1)-C(8)-C(9)$ $107.1(4)$ $N(1)-C(8)-C(5)$ $126.9(4)$ $C(9)-C(8)-C(5)$ $125.9(4)$ $C(4)-C(5)-C(6)$ $115.4(4)$ $C(4)-C(5)-C(8)$ $127.1(4)$ $C(4)-C(5)-C(8)$ $127.1(4)$ $C(6)-C(5)-C(8)$ $117.4(4)$	C(10)-C(12)	1.442(6)	
O(1)-C(1)1.411(8) $C(12)-C(17)$ 1.322(7) $C(12)-C(13)$ 1.356(7) $C(2)-C(3)$ 1.338(7) $C(2)-C(7)$ 1.376(7) $C(3)-C(4)$ 1.343(6) $C(6)-C(7)$ 1.330(6) $C(15)-F(2)$ 1.278(9) $C(15)-C(16)$ 1.285(8) $C(15)-C(14)$ 1.357(8) $C(13)-C(14)$ 1.355(7) $C(17)-C(16)$ 1.363(7) $B(1)-F(1)#1$ 1.349(4) $B(1)-F(1)#1$ 1.349(4) $B(1)-N(1)#1$ 107.1(3) $C(8)-N(1)-C(11)$ 107.1(3) $C(8)-N(1)-C(11)$ 107.1(3) $C(8)-N(1)-C(11)$ 107.1(3) $C(8)-N(1)-C(11)$ 107.1(3) $C(11)-N(1)-B(1)$ 122.4(3) $C(11)-N(1)-B(1)$ 122.4(3) $C(11)-N(1)-B(1)$ 124.1(4) $N(2)-C(11)-N(1)$ 124.1(4) $N(2)-C(11)-N(1)$ 126.4(4) $N(1)-C(8)-C(9)$ 107.1(4) $N(1)-C(8)-C(9)$ 107.1(4) $N(1)-C(8)-C(5)$ 126.9(4) $C(9)-C(8)-C(5)$ 125.9(4) $C(4)-C(5)-C(6)$ 115.4(4) $C(4)-C(5)-C(8)$ 127.1(4) $C(4)-C(5)-C(8)$ 127.1(4) $C(6)-C(5)-C(8)$ 127.1(4) $C(6)-C(5)-C(8)$ 127.1(4)	O(1)-C(2)	1.322(5)	
C(12)-C(17) $1.322(7)$ $C(12)-C(13)$ $1.356(7)$ $C(2)-C(3)$ $1.338(7)$ $C(2)-C(7)$ $1.376(7)$ $C(3)-C(4)$ $1.343(6)$ $C(6)-C(7)$ $1.330(6)$ $C(15)-F(2)$ $1.278(9)$ $C(15)-C(16)$ $1.285(8)$ $C(15)-C(14)$ $1.357(8)$ $C(13)-C(14)$ $1.355(7)$ $C(17)-C(16)$ $1.363(7)$ $B(1)-F(1)#1$ $1.349(4)$ $B(1)-F(1)#1$ $1.518(5)$ $C(8)-N(1)-C(11)$ $107.1(3)$ $C(8)-N(1)-B(1)$ $122.4(3)$ $C(11)-N(1)-B(1)$ $122.4(3)$ $C(11)-N(1)-B(1)$ $124.1(4)$ $N(2)-C(11)-N(1)$ $126.4(4)$ $N(1)-C(11)-C(10)$ $109.5(4)$ $N(1)-C(8)-C(5)$ $125.9(4)$ $C(9)-C(8)-C(5)$ $125.9(4)$ $C(4)-C(5)-C(6)$ $115.4(4)$ $C(4)-C(5)-C(8)$ $127.1(4)$	O(1)-C(1)	1.411(8)	
C(12)-C(13)1.356(7) $C(2)-C(3)$ 1.338(7) $C(2)-C(7)$ 1.376(7) $C(3)-C(4)$ 1.343(6) $C(6)-C(7)$ 1.330(6) $C(15)-F(2)$ 1.278(9) $C(15)-C(16)$ 1.285(8) $C(15)-C(14)$ 1.357(8) $C(13)-C(14)$ 1.355(7) $C(17)-C(16)$ 1.363(7) $B(1)-F(1)#1$ 1.349(4) $B(1)-F(1)#1$ 1.518(5) $C(8)-N(1)-C(11)$ 107.1(3) $C(8)-N(1)-B(1)$ 130.5(3) $C(11)-N(1)-B(1)$ 122.4(3) $C(11)-N(1)-B(1)$ 124.1(4) $N(2)-C(11)-N(1)$ 126.4(4) $N(1)-C(11)-C(10)$ 109.5(4) $N(1)-C(11)-C(10)$ 109.5(4) $N(1)-C(8)-C(5)$ 126.9(4) $C(9)-C(8)-C(5)$ 125.9(4) $C(4)-C(5)-C(6)$ 115.4(4) $C(4)-C(5)-C(8)$ 127.1(4) $C(6)-C(5)-C(8)$ 117.4(4)	C(12)-C(17)	1.322(7)	
C(2)- $C(3)$ 1.338(7) $C(2)$ - $C(7)$ 1.376(7) $C(3)$ - $C(4)$ 1.343(6) $C(6)$ - $C(7)$ 1.330(6) $C(15)$ - $F(2)$ 1.278(9) $C(15)$ - $C(16)$ 1.285(8) $C(15)$ - $C(14)$ 1.357(8) $C(13)$ - $C(14)$ 1.355(7) $C(17)$ - $C(16)$ 1.363(7) $B(1)$ - $F(1)$ #11.349(4) $B(1)$ - $F(1)$ #11.518(5) $C(8)$ - $N(1)$ - $C(11)$ 107.1(3) $C(8)$ - $N(1)$ - $B(1)$ 122.4(3) $C(11)$ - $N(1)$ - $B(1)$ 124.1(4) $N(2)$ - $C(11)$ = $N(1)$ 126.4(4) $N(1)$ - $C(10)$ 109.5(4) $N(1)$ - $C(10)$ 109.5(4) $N(1)$ - $C(5)$ 126.9(4) $C(9)$ - $C(5)$ 125.9(4) $C(4)$ - $C(5)$ - $C(6)$ 115.4(4) $C(4)$ - $C(5)$ - $C(8)$ 127.1(4) $C(6)$ - $C(5)$ - $C(8)$ 117.4(4)	C(12)-C(13)	1.356(7)	
C(2)- $C(7)$ 1.376(7) $C(3)$ - $C(4)$ 1.343(6) $C(6)$ - $C(7)$ 1.330(6) $C(15)$ - $F(2)$ 1.278(9) $C(15)$ - $C(16)$ 1.285(8) $C(13)$ - $C(14)$ 1.357(8) $C(13)$ - $C(14)$ 1.355(7) $C(17)$ - $C(16)$ 1.363(7) $B(1)$ - $F(1)$ #11.349(4) $B(1)$ - $N(1)$ #11.518(5) $C(8)$ - $N(1)$ - $C(11)$ 107.1(3) $C(8)$ - $N(1)$ - $B(1)$ 122.4(3) $C(11)$ - $N(1)$ - $B(1)$ 122.4(3) $C(11)$ - $N(1)$ - $B(1)$ 124.1(4) $N(2)$ - $C(11)$ = $N(1)$ 126.4(4) $N(1)$ - $C(10)$ 109.5(4) $N(1)$ - $C(10)$ 109.5(4) $N(1)$ - $C(5)$ 126.9(4) $C(9)$ - $C(5)$ 125.9(4) $C(4)$ - $C(5)$ - $C(6)$ 115.4(4) $C(4)$ - $C(5)$ - $C(8)$ 127.1(4) $C(6)$ - $C(5)$ - $C(8)$ 117.4(4)	C(2)-C(3)	1.338(7)	
C(3)- $C(4)$ 1.343(6) $C(6)$ - $C(7)$ 1.330(6) $C(15)$ - $F(2)$ 1.278(9) $C(15)$ - $C(16)$ 1.285(8) $C(15)$ - $C(14)$ 1.357(8) $C(13)$ - $C(14)$ 1.355(7) $C(17)$ - $C(16)$ 1.363(7) $B(1)$ - $F(1)$ #11.349(4) $B(1)$ - $F(1)$ #11.349(4) $B(1)$ - $N(1)$ #11.518(5) $C(8)$ - $N(1)$ - $C(11)$ 107.1(3) $C(8)$ - $N(1)$ - $C(11)$ 107.1(3) $C(8)$ - $N(1)$ - $B(1)$ 122.4(3) $C(11)$ - $N(2)$ - $C(11)$ #1119.8(5) $N(2)$ - $C(11)$ - $N(1)$ 124.1(4) $N(2)$ - $C(11)$ - $N(1)$ 126.4(4) $N(1)$ - $C(10)$ 126.4(4) $N(1)$ - $C(10)$ 109.5(4) $N(1)$ - $C(1)$ - $C(10)$ 109.5(4) $N(1)$ - $C(8)$ - $C(5)$ 126.9(4) $C(9)$ - $C(5)$ - $C(6)$ 115.4(4) $C(4)$ - $C(5)$ - $C(6)$ 115.4(4) $C(4)$ - $C(5)$ - $C(8)$ 127.1(4) $C(6)$ - $C(5)$ - $C(8)$ 117.4(4)	C(2)-C(7)	1.376(7)	
C(6)-C(7)1.330(6) $C(15)-F(2)$ 1.278(9) $C(15)-C(16)$ 1.285(8) $C(15)-C(14)$ 1.357(8) $C(13)-C(14)$ 1.355(7) $C(17)-C(16)$ 1.363(7) $B(1)-F(1)#1$ 1.349(4) $B(1)-N(1)#1$ 1.518(5) $C(8)-N(1)-C(11)$ 107.1(3) $C(8)-N(1)-B(1)$ 130.5(3) $C(11)-N(1)-B(1)$ 122.4(3) $C(11)-N(1)-B(1)$ 124.1(4) $N(2)-C(11)+N(1)$ 124.1(4) $N(2)-C(11)-C(10)$ 109.5(4) $N(1)-C(10)$ 109.5(4) $N(1)-C(10)$ 109.5(4) $N(1)-C(8)-C(5)$ 126.9(4) $C(9)-C(8)-C(5)$ 125.9(4) $C(4)-C(5)-C(6)$ 115.4(4) $C(4)-C(5)-C(8)$ 127.1(4) $C(6)-C(5)-C(8)$ 117.4(4)	C(3)-C(4)	1.343(6)	
C(15)- $F(2)$ $1.278(9)$ $C(15)$ - $C(16)$ $1.285(8)$ $C(13)$ - $C(14)$ $1.357(8)$ $C(13)$ - $C(14)$ $1.355(7)$ $C(17)$ - $C(16)$ $1.363(7)$ $B(1)$ - $F(1)$ #1 $1.349(4)$ $B(1)$ - $F(1)$ #1 $1.3149(4)$ $B(1)$ - $N(1)$ #1 $1.518(5)$ $C(8)$ - $N(1)$ - $C(11)$ $107.1(3)$ $C(8)$ - $N(1)$ - $B(1)$ $122.4(3)$ $C(11)$ - $N(2)$ - $C(11)$ #1 $119.8(5)$ $N(2)$ - $C(11)$ - $N(1)$ $124.1(4)$ $N(2)$ - $C(11)$ - $C(10)$ $126.4(4)$ $N(1)$ - $C(10)$ $109.5(4)$ $N(1)$ - $C(1)$ - $C(5)$ $126.9(4)$ $C(9)$ - $C(5)$ $125.9(4)$ $C(4)$ - $C(5)$ - $C(6)$ $115.4(4)$ $C(4)$ - $C(5)$ - $C(8)$ $127.1(4)$ $C(6)$ - $C(5)$ - $C(8)$ $117.4(4)$	C(6)-C(7)	1.330(6)	
C(15)-C(16) $1.285(8)$ $C(13)-C(14)$ $1.357(8)$ $C(13)-C(14)$ $1.355(7)$ $C(17)-C(16)$ $1.363(7)$ $B(1)-F(1)#1$ $1.349(4)$ $B(1)-N(1)#1$ $1.518(5)$ $C(8)-N(1)-C(11)$ $107.1(3)$ $C(8)-N(1)-B(1)$ $122.4(3)$ $C(11)-N(1)-B(1)$ $122.4(3)$ $C(11)-N(2)-C(11)#1$ $119.8(5)$ $N(2)-C(11)-N(1)$ $126.4(4)$ $N(1)-C(11)-C(10)$ $126.4(4)$ $N(1)-C(11)-C(10)$ $109.5(4)$ $N(1)-C(8)-C(9)$ $107.1(4)$ $N(1)-C(8)-C(5)$ $125.9(4)$ $C(9)-C(8)-C(5)$ $125.9(4)$ $C(4)-C(5)-C(6)$ $115.4(4)$ $C(4)-C(5)-C(8)$ $127.1(4)$ $C(6)-C(5)-C(8)$ $117.4(4)$	C(15)-F(2)	1.278(9)	
C(15)-C(14) $1.357(8)$ $C(13)-C(14)$ $1.355(7)$ $C(17)-C(16)$ $1.363(7)$ $B(1)-F(1)#1$ $1.349(4)$ $B(1)-N(1)#1$ $1.518(5)$ $C(8)-N(1)-C(11)$ $107.1(3)$ $C(8)-N(1)-B(1)$ $130.5(3)$ $C(11)-N(1)-B(1)$ $122.4(3)$ $C(11)-N(1)-B(1)$ $122.4(3)$ $C(11)-N(2)-C(11)#1$ $119.8(5)$ $N(2)-C(11)-N(1)$ $124.1(4)$ $N(2)-C(11)-C(10)$ $126.4(4)$ $N(1)-C(8)-C(9)$ $107.1(4)$ $N(1)-C(8)-C(5)$ $126.9(4)$ $C(9)-C(8)-C(5)$ $125.9(4)$ $C(4)-C(5)-C(6)$ $115.4(4)$ $C(4)-C(5)-C(8)$ $127.1(4)$ $C(6)-C(5)-C(8)$ $117.4(4)$	C(15)-C(16)	1.285(8)	
C(13)-C(14) $1.355(7)$ $C(17)-C(16)$ $1.363(7)$ $B(1)-F(1)#1$ $1.349(4)$ $B(1)-N(1)#1$ $1.518(5)$ $C(8)-N(1)-C(11)$ $107.1(3)$ $C(8)-N(1)-B(1)$ $120.5(3)$ $C(11)-N(1)-B(1)$ $122.4(3)$ $C(11)-N(1)-B(1)$ $122.4(3)$ $C(11)-N(2)-C(11)#1$ $119.8(5)$ $N(2)-C(11)-N(1)$ $124.1(4)$ $N(2)-C(11)-N(1)$ $126.4(4)$ $N(1)-C(8)-C(9)$ $107.1(4)$ $N(1)-C(8)-C(5)$ $126.9(4)$ $C(9)-C(8)-C(5)$ $125.9(4)$ $C(4)-C(5)-C(6)$ $115.4(4)$ $C(4)-C(5)-C(8)$ $127.1(4)$ $C(6)-C(5)-C(8)$ $117.4(4)$	C(15)-C(14)	1.357(8)	
C(17)-C(16)1.363(7) $B(1)-F(1)#1$ 1.349(4) $B(1)-N(1)#1$ 1.518(5) $C(8)-N(1)-C(11)$ 107.1(3) $C(8)-N(1)-B(1)$ 130.5(3) $C(11)-N(1)-B(1)$ 122.4(3) $C(11)-N(2)-C(11)#1$ 119.8(5) $N(2)-C(11)-N(1)$ 124.1(4) $N(2)-C(11)-C(10)$ 126.4(4) $N(1)-C(1)-C(10)$ 109.5(4) $N(1)-C(8)-C(9)$ 107.1(4) $N(1)-C(8)-C(5)$ 126.9(4) $C(9)-C(8)-C(5)$ 125.9(4) $C(4)-C(5)-C(6)$ 115.4(4) $C(4)-C(5)-C(8)$ 127.1(4) $C(6)-C(5)-C(8)$ 117.4(4)	C(13)-C(14)	1.355(7)	
B(1)-F(1)#1 $1.349(4)$ $B(1)-N(1)#1$ $1.518(5)$ $C(8)-N(1)-C(11)$ $107.1(3)$ $C(8)-N(1)-B(1)$ $130.5(3)$ $C(11)-N(1)-B(1)$ $122.4(3)$ $C(11)-N(2)-C(11)#1$ $119.8(5)$ $N(2)-C(11)-N(1)$ $124.1(4)$ $N(2)-C(11)-C(10)$ $126.4(4)$ $N(1)-C(11)-C(10)$ $109.5(4)$ $N(1)-C(8)-C(9)$ $107.1(4)$ $N(1)-C(8)-C(5)$ $126.9(4)$ $C(9)-C(8)-C(5)$ $125.9(4)$ $C(4)-C(5)-C(6)$ $115.4(4)$ $C(4)-C(5)-C(8)$ $127.1(4)$ $C(6)-C(5)-C(8)$ $117.4(4)$	C(17)-C(16)	1.363(7)	
B(1)-N(1)#1 $1.518(5)$ $C(8)-N(1)-C(11)$ $107.1(3)$ $C(8)-N(1)-B(1)$ $130.5(3)$ $C(11)-N(1)-B(1)$ $122.4(3)$ $C(11)-N(2)-C(11)#1$ $119.8(5)$ $N(2)-C(11)-N(1)$ $124.1(4)$ $N(2)-C(11)-N(1)$ $126.4(4)$ $N(1)-C(11)-C(10)$ $109.5(4)$ $N(1)-C(11)-C(10)$ $109.5(4)$ $N(1)-C(8)-C(9)$ $107.1(4)$ $N(1)-C(8)-C(5)$ $126.9(4)$ $C(9)-C(8)-C(5)$ $125.9(4)$ $C(4)-C(5)-C(6)$ $115.4(4)$ $C(4)-C(5)-C(8)$ $127.1(4)$ $C(6)-C(5)-C(8)$ $117.4(4)$	B(1)-F(1)#1	1.349(4)	
C(8)-N(1)-C(11)107.1(3) $C(8)$ -N(1)-B(1)130.5(3) $C(11)$ -N(1)-B(1)122.4(3) $C(11)$ -N(2)-C(11)#1119.8(5)N(2)-C(11)-N(1)124.1(4)N(2)-C(11)-C(10)126.4(4)N(1)-C(11)-C(10)109.5(4)N(1)-C(8)-C(9)107.1(4)N(1)-C(8)-C(5)126.9(4) $C(9)$ -C(8)-C(5)125.9(4) $C(4)$ -C(5)-C(6)115.4(4) $C(4)$ -C(5)-C(8)127.1(4) $C(6)$ -C(5)-C(8)117.4(4)	B(1)-N(1)#1	1.518(5)	
C(8)-N(1)- $C(11)$ 107.1(3) $C(8)$ -N(1)-B(1)130.5(3) $C(11)$ -N(1)-B(1)122.4(3) $C(11)$ -N(2)- $C(11)$ #1119.8(5)N(2)- $C(11)$ -N(1)124.1(4)N(2)- $C(11)$ - $C(10)$ 126.4(4)N(1)- $C(11)$ - $C(10)$ 109.5(4)N(1)- $C(8)$ - $C(9)$ 107.1(4)N(1)- $C(8)$ - $C(5)$ 126.9(4) $C(9)$ - $C(8)$ - $C(5)$ 125.9(4) $C(4)$ - $C(5)$ - $C(6)$ 115.4(4) $C(4)$ - $C(5)$ - $C(8)$ 127.1(4) $C(6)$ - $C(5)$ - $C(8)$ 117.4(4)			
C(8)-N(1)-B(1)130.5(3) $C(11)$ -N(1)-B(1)122.4(3) $C(11)$ -N(2)-C(11)#1119.8(5)N(2)-C(11)-N(1)124.1(4)N(2)-C(11)-C(10)126.4(4)N(1)-C(11)-C(10)109.5(4)N(1)-C(8)-C(9)107.1(4)N(1)-C(8)-C(5)126.9(4)C(9)-C(8)-C(5)125.9(4)C(4)-C(5)-C(6)115.4(4)C(4)-C(5)-C(8)127.1(4)C(6)-C(5)-C(8)117.4(4)	C(8)-N(1)-C(11)	107.1(3)	
C(11)-N(1)-B(1) $122.4(3)$ $C(11)-N(2)-C(11)#1$ $119.8(5)$ $N(2)-C(11)-N(1)$ $124.1(4)$ $N(2)-C(11)-C(10)$ $126.4(4)$ $N(1)-C(11)-C(10)$ $109.5(4)$ $N(1)-C(8)-C(9)$ $107.1(4)$ $N(1)-C(8)-C(5)$ $126.9(4)$ $C(9)-C(8)-C(5)$ $125.9(4)$ $C(4)-C(5)-C(6)$ $115.4(4)$ $C(4)-C(5)-C(8)$ $127.1(4)$ $C(6)-C(5)-C(8)$ $117.4(4)$	C(8)-N(1)-B(1)	130.5(3)	
C(11)-N(2)-C(11)#1 $119.8(5)$ $N(2)-C(11)-N(1)$ $124.1(4)$ $N(2)-C(11)-C(10)$ $126.4(4)$ $N(1)-C(11)-C(10)$ $109.5(4)$ $N(1)-C(8)-C(9)$ $107.1(4)$ $N(1)-C(8)-C(5)$ $126.9(4)$ $C(9)-C(8)-C(5)$ $125.9(4)$ $C(4)-C(5)-C(6)$ $115.4(4)$ $C(4)-C(5)-C(8)$ $127.1(4)$ $C(6)-C(5)-C(8)$ $117.4(4)$	C(11)-N(1)-B(1)	122.4(3)	
N(2)-C(11)-N(1) $124.1(4)$ $N(2)-C(11)-C(10)$ $126.4(4)$ $N(1)-C(11)-C(10)$ $109.5(4)$ $N(1)-C(8)-C(9)$ $107.1(4)$ $N(1)-C(8)-C(5)$ $126.9(4)$ $C(9)-C(8)-C(5)$ $125.9(4)$ $C(4)-C(5)-C(6)$ $115.4(4)$ $C(4)-C(5)-C(8)$ $127.1(4)$ $C(6)-C(5)-C(8)$ $117.4(4)$	C(11)-N(2)-C(11)#1	119.8(5)	
N(2)-C(11)-C(10)126.4(4) $N(1)-C(11)-C(10)$ 109.5(4) $N(1)-C(8)-C(9)$ 107.1(4) $N(1)-C(8)-C(5)$ 126.9(4) $C(9)-C(8)-C(5)$ 125.9(4) $C(4)-C(5)-C(6)$ 115.4(4) $C(4)-C(5)-C(8)$ 127.1(4) $C(6)-C(5)-C(8)$ 117.4(4)	N(2)-C(11)-N(1)	124.1(4)	
N(1)-C(11)-C(10)109.5(4) $N(1)-C(8)-C(9)$ 107.1(4) $N(1)-C(8)-C(5)$ 126.9(4) $C(9)-C(8)-C(5)$ 125.9(4) $C(4)-C(5)-C(6)$ 115.4(4) $C(4)-C(5)-C(8)$ 127.1(4) $C(6)-C(5)-C(8)$ 117.4(4)	N(2)-C(11)-C(10)	126.4(4)	
N(1)-C(8)-C(9)107.1(4) $N(1)-C(8)-C(5)$ 126.9(4) $C(9)-C(8)-C(5)$ 125.9(4) $C(4)-C(5)-C(6)$ 115.4(4) $C(4)-C(5)-C(8)$ 127.1(4) $C(6)-C(5)-C(8)$ 117.4(4)	N(1)-C(11)-C(10)	109.5(4)	
N(1)-C(8)-C(5)126.9(4) $C(9)-C(8)-C(5)$ 125.9(4) $C(4)-C(5)-C(6)$ 115.4(4) $C(4)-C(5)-C(8)$ 127.1(4) $C(6)-C(5)-C(8)$ 117.4(4)	N(1)-C(8)-C(9)	107.1(4)	
C(9)-C(8)-C(5)125.9(4) $C(4)-C(5)-C(6)$ 115.4(4) $C(4)-C(5)-C(8)$ 127.1(4) $C(6)-C(5)-C(8)$ 117.4(4)	N(1)-C(8)-C(5)	126.9(4)	
C(4)-C(5)-C(6)115.4(4)C(4)-C(5)-C(8)127.1(4)C(6)-C(5)-C(8)117.4(4)	C(9)-C(8)-C(5)	125.9(4)	
C(4)-C(5)-C(8) 127.1(4) C(6)-C(5)-C(8) 117.4(4)	C(4)-C(5)-C(6)	115.4(4)	
C(6)-C(5)-C(8) 117.4(4)	C(4)-C(5)-C(8)	127.1(4)	
	C(6)-C(5)-C(8)	117.4(4)	

Table S3. Bond lengths [Å] and angles [°].

C(9)-C(10)-C(11)	105.0(4)
C(9)-C(10)-C(12)	128.1(4)
C(11)-C(10)-C(12)	126.9(4)
C(2)-O(1)-C(1)	118.4(5)
C(10)-C(9)-C(8)	111.3(4)
C(17)-C(12)-C(13)	117.9(5)
C(17)-C(12)-C(10)	119.3(4)
C(13)-C(12)-C(10)	122.6(4)
O(1)-C(2)-C(3)	115.4(5)
O(1)-C(2)-C(7)	124.6(5)
C(3)-C(2)-C(7)	120.0(4)
C(2)-C(3)-C(4)	119.9(5)
C(3)-C(4)-C(5)	122.8(4)
C(7)-C(6)-C(5)	122.3(5)
F(2)-C(15)-C(16)	114.7(7)
F(2)-C(15)-C(14)	120.4(6)
C(16)-C(15)-C(14)	124.7(5)
C(14)-C(13)-C(12)	122.0(5)
C(12)-C(17)-C(16)	121.9(5)
C(6)-C(7)-C(2)	119.5(5)
F(1)-B(1)-F(1)#1	111.8(5)
F(1)-B(1)-N(1)	109.19(16)
F(1)#1-B(1)-N(1)	109.74(16)
F(1)-B(1)-N(1)#1	109.74(16)
F(1)#1-B(1)-N(1)#1	109.18(16)
N(1)-B(1)-N(1)#1	107.1(5)
C(15)-C(16)-C(17)	117.7(5)
C(13)-C(14)-C(15)	115.5(5)

Symmetry transformations used to generate equivalent atoms:

^{#1 -}x+1,-y+1/2,z+0

	U ¹¹	U ²²	U ³³	U ²³	U ¹³	U ¹²
F(1)	69(2)	65(2)	70(2)	-1(1)	-10(1)	2(1)
N(1)	65(2)	49(2)	53(2)	2(1)	1(2)	3(1)
N(2)	58(3)	48(2)	65(3)	0	0	0(2)
C(11)	64(2)	57(2)	48(2)	-1(2)	1(2)	3(2)
C(8)	61(2)	53(2)	61(2)	4(2)	4(2)	3(2)
C(5)	65(2)	54(2)	59(2)	5(2)	-6(2)	7(2)
C(10)	65(3)	49(2)	61(2)	4(2)	6(2)	1(2)
O(1)	103(3)	92(3)	72(2)	16(2)	-15(2)	6(2)
C(9)	77(3)	54(2)	63(2)	-2(2)	2(2)	7(2)
C(12)	66(3)	58(2)	56(2)	-1(2)	6(2)	7(2)
C(2)	72(3)	61(3)	73(3)	11(2)	-8(2)	-2(2)
C(3)	88(3)	66(3)	60(2)	3(2)	4(2)	4(2)
C(4)	86(3)	64(3)	62(3)	2(2)	1(2)	15(2)
C(6)	99(4)	71(3)	66(3)	1(2)	-1(3)	27(3)
C(15)	123(5)	88(4)	51(2)	-10(3)	9(3)	15(3)
C(13)	86(4)	76(3)	74(3)	5(2)	3(3)	4(3)
C(17)	115(4)	67(3)	71(3)	2(2)	-6(3)	7(3)
C(7)	94(4)	70(3)	78(3)	11(3)	-5(3)	29(3)
B(1)	53(3)	61(4)	52(3)	v 0	0	8(3)
C(16)	133(5)	69(3)	68(3)	-14(3)	-4(3)	21(3)
C(14)	111(4)	89(4)	62(3)	7(3)	10(3)	0(3)
F(2)	415(14)	190(7)	204(7)	-10(6)	73(7)	67(8)
C(1)	156(8)	139(6)	132(6)	54(5)	-13(5)	64(6)

Table S4. Anisotropic displacement parameters (Å²x 10³). The anisotropic displacement factor exponent takes the form: $-2\pi^2$ [$h^2a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}$]

4... 156(8)

	Х	У	Z	U(eq)
	10.00	1000	10.67	
H(9)	4060	4889	1367	78
H(3)	4370	3990	-1513	86
H(4)	4752	3436	-524	85
H(6)	3565	5222	438	94
H(13)	4050	3027	2902	95
H(17)	4743	5259	2414	101
H(7)	3179	5770	-549	97
H(16)	4698	5646	3522	108
H(14)	3983	3401	4015	105
H(1A)	3426	6401	-1664	213
H(1B)	2622	5901	-1498	213
H(1C)	2909	6003	-2245	213

Table S5. Hydrogen coordinates (Å x 10^4) and isotropic displacement parameters (Å²x 10^3).

Table S6. Torsion angles [°].

C(11)#1-N(2)-C(11)-N(1)	0.8(3)
C(11)#1-N(2)-C(11)-C(10)	179.9(5)
C(8)-N(1)-C(11)-N(2)	177.2(4)
B(1)-N(1)-C(11)-N(2)	-1.5(6)
C(8)-N(1)-C(11)-C(10)	-2.0(5)
B(1)-N(1)-C(11)-C(10)	179.2(3)
C(11)-N(1)-C(8)-C(9)	2.1(5)
B(1)-N(1)-C(8)-C(9)	-179.3(3)
C(11)-N(1)-C(8)-C(5)	-175.4(4)
B(1)-N(1)-C(8)-C(5)	3.3(7)
N(1)-C(8)-C(5)-C(4)	-12.5(8)
C(9)-C(8)-C(5)-C(4)	170.5(5)
N(1)-C(8)-C(5)-C(6)	167.4(5)
C(9)-C(8)-C(5)-C(6)	-9.6(7)
N(2)-C(11)-C(10)-C(9)	-178.1(4)
N(1)-C(11)-C(10)-C(9)	1.1(5)
N(2)-C(11)-C(10)-C(12)	3.8(7)
N(1)-C(11)-C(10)-C(12)	-176.9(4)
C(11)-C(10)-C(9)-C(8)	0.2(6)
C(12)-C(10)-C(9)-C(8)	178.2(5)
N(1)-C(8)-C(9)-C(10)	-1.4(6)
C(5)-C(8)-C(9)-C(10)	176.0(4)
C(9)-C(10)-C(12)-C(17)	-34.6(8)
C(11)-C(10)-C(12)-C(17)	143.0(5)
C(9)-C(10)-C(12)-C(13)	140.8(5)
C(11)-C(10)-C(12)-C(13)	-41.5(7)
C(1)-O(1)-C(2)-C(3)	-179.4(6)
C(1)-O(1)-C(2)-C(7)	2.2(8)
O(1)-C(2)-C(3)-C(4)	-179.6(5)
C(7)-C(2)-C(3)-C(4)	-1.2(8)
C(2)-C(3)-C(4)-C(5)	0.7(8)
C(6)-C(5)-C(4)-C(3)	-0.4(8)
C(8)-C(5)-C(4)-C(3)	179.5(5)
C(4)-C(5)-C(6)-C(7)	0.5(8)
C(8)-C(5)-C(6)-C(7)	-179.4(5)
C(17)-C(12)-C(13)-C(14)	-3.2(8)
C(10)-C(12)-C(13)-C(14)	-178.6(5)
C(13)-C(12)-C(17)-C(16)	3.6(8)
C(10)-C(12)-C(17)-C(16)	179.2(5)
C(5)-C(6)-C(7)-C(2)	-1.0(9)
O(1)-C(2)-C(7)-C(6)	179.6(5)
C(3)-C(2)-C(7)-C(6)	1.3(8)

C(8)-N(1)-B(1)-F(1)	-59.0(5)
C(11)-N(1)-B(1)-F(1)	119.5(4)
C(8)-N(1)-B(1)-F(1)#1	63.8(5)
C(11)-N(1)-B(1)-F(1)#1	-117.7(4)
C(8)-N(1)-B(1)-N(1)#1	-177.8(4)
C(11)-N(1)-B(1)-N(1)#1	0.7(3)
F(2)-C(15)-C(16)-C(17)	172.1(7)
C(14)-C(15)-C(16)-C(17)	-3.1(10)
C(12)-C(17)-C(16)-C(15)	-0.6(9)
C(12)-C(13)-C(14)-C(15)	-0.2(8)
F(2)-C(15)-C(14)-C(13)	-171.5(8)
C(16)-C(15)-C(14)-C(13)	3.4(10)

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,-y+1/2,z+0

4. Ground state geometries in gas phase (M062X/6-311+G(2d,p))

Compound 3 E= -1819.96788515 a.u.

COII	ipoullu 3 L1819.90	786515 a.u.		
5	-2.0188870	0.0138560	0.3350060	
9	-3.0272740	0.0012940	-0.5961060	
9	-2.5129360	0.0474810	1.6404940	
7	-1.0960220	-1.2445260	0.1814100	
6	0.2921760	-1.1519410	0.2082710	
7	0.9587420	-0.0164310	0.1877800	
6	0.3141300	1.1296400	0.1231910	
7	-1.0732940	1.2479980	0.1240010	
6	-1.4122420	-2.5482270	0.0326460	
6	-0.2245080	-3.3207940	-0.0368340	
6	0.8550800	-2.4661510	0.0929870	
6	-1.3685150	2.5540520	-0.0447040	
6	-0.1679310	3.3023500	-0.1490980	
6	0.8988090	2.4297490	-0.0378740	
6	2.2809550	-2.7960780	0.0727170	
6	2.7155920	-3.9553720	-0.5873310	
1	1.9928900	-4.5834250	-1.0990190	
6	4.0601840	-4.2989880	-0.6222400	
1	4.4100290	-5.1879280	-1.1347680	
6	4.9720160	-3.4661390	0.0107130	
6	4.5830720	-2.3120230	0.6749250	
1	5.3303210	-1.6962980	1.1631050	
6	3.2337860	-1.9825340	0.7069900	
1	2.9134640	-1.0898400	1.2313400	
6	2.3286280	2.7507620	-0.0571120	
6	3.2955780	1.8170870	-0.4643660	
1	2.9875520	0.8267220	-0.7775630	
6	4.6442640	2.1506470	-0.4747810	
1	5.4015070	1.4413710	-0.7902960	
6	5.0203160	3.4260920	-0.0804410	
6	4.0950040	4.3777020	0.3237250	
1	4.4337530	5.3607660	0.6305750	
6	2.7507290	4.0310130	0.3327110	
1	2.0179190	4.7575270	0.6699120	
6	-2.7698250	-3.0990940	-0.0335910	
6	-2.9885080	-4.2258970	-0.8405540	
6	-4.2485860	-4.8060200	-0.9151610	
1	-4.4074570	-5.6692630	-1.5533020	
6	-5.3039470	-4.2761640	-0.1747830	
6	-5.0912000	-3.1640110	0.6377100	

1	-5.9081720	-2.7550160	1.2234600	
6	-3.8347450	-2.5740630	0.7112450	
1	-3.6713140	-1.7222550	1.3599050	
6	-2.7165050	3.1278230	-0.1253640	
6	-2.9140810	4.2366160	-0.9625800	
6	-4.1631740	4.8375490	-1.0546580	
1	-4.3052180	5.6858690	-1.7163550	
6	-5.2291240	4.3473350	-0.3022430	
6	-5.0374720	3.2537180	0.5398660	
1	-5.8623730	2.8751300	1.1349020	
6	-3.7920930	2.6428740	0.6312440	
1	-3.6460660	1.8058900	1.3025780	
1	-2.0896060	4.6089000	-1.5630850	
1	-2.1709050	-4.6289810	-1.4305910	
1	-0.1258300	4.3736710	-0.2877690	
1	-0.2011370	-4.3993820	-0.1079480	
9	6.3217680	3.7514770	-0.0896120	
1	-6.2884870	-4.7298990	-0.2294940	
1	-6.2050900	4.8174110	-0.3708510	
9	6.2734970	-3.7889890	-0.0207170	
Comp	ound 4 E= -2049.00	336427 a.u.		
5	-1.3053530	0.0084970	0.4414670	

Compound 4 E= -2049.00336427 a.u.

5	-1.3053530	0.0084970	0.4414670
9	-2.3325010	-0.0000150	-0.4713860
9	-1.7812100	0.0373940	1.7554680
7	-0.3893860	-1.2500670	0.2669160
6	0.9990330	-1.1578480	0.2497870
7	1.6662870	-0.0229310	0.2131600
6	1.0201350	1.1236980	0.1749680
7	-0.3664650	1.2435030	0.2191270
6	-0.7132420	-2.5547170	0.1256580
6	0.4741620	-3.3258650	0.0169240
6	1.5566540	-2.4716160	0.1126310
6	-0.6678160	2.5522150	0.0674590
6	0.5326270	3.2983160	-0.0687700
6	1.6002680	2.4239010	0.0036240
6	2.9815560	-2.8020070	0.0459330
6	3.3952810	-3.9585820	-0.6318780
1	2.6566430	-4.5847320	-1.1228110
6	4.7382340	-4.3021580	-0.7106500
1	5.0715080	-5.1892070	-1.2373730
6	5.6698110	-3.4717240	-0.1040610
6	5.3020510	-2.3201960	0.5762910

1	6.0644150	-1.7058620	1.0424310	
6	3.9543090	-1.9910290	0.6524690	
1	3.6505290	-1.0997820	1.1889790	
6	3.0298350	2.7436710	-0.0558640	
6	3.9824480	1.8126350	-0.5008980	
1	3.6630810	0.8251800	-0.8119710	
6	5.3308660	2.1444620	-0.5500600	
1	6.0768490	1.4367620	-0.8946780	
6	5.7211000	3.4157980	-0.1565660	
6	4.8102310	4.3647280	0.2845130	
1	5.1597840	5.3445850	0.5896100	
6	3.4661770	4.0195240	0.3322410	
1	2.7453460	4.7438650	0.6987430	
6	-2.0668750	-3.1052050	0.0991910	
6	-2.3045050	-4.2559290	-0.6626050	
6	-3.5601100	-4.8493440	-0.7143680	
1	-3.7082890	-5.7293400	-1.3281250	
6	-4.6100100	-4.2935090	0.0228290	
6	-4.3832220	-3.1491560	0.8005810	
1	-5.2096250	-2.7442820	1.3749400	
6	-3.1337550	-2.5618650	0.8378810	
1	-2.9716460	-1.6919520	1.4619440	
8	-5.8678130	-4.7872380	0.0518850	
6	-6.1393700	-5.9469900	-0.7154620	
1	-5.9643120	-5.7641040	-1.7811800	
1	-5.5254480	-6.7913850	-0.3836780	
1	-7.1917690	-6.1752600	-0.5529840	
6	-2.0114450	3.1278000	0.0296300	
6	-2.2259380	4.2682360	-0.7545960	
6	-3.4698820	4.8842870	-0.8209850	
1	-3.5996860	5.7548220	-1.4521720	
6	-4.5320500	4.3627580	-0.0764090	
6	-4.3285850	3.2295290	0.7234750	
1	-5.1638300	2.8510090	1.3030330	
6	-3.0905360	2.6193490	0.7753940	
1	-2.9475130	1.7585960	1.4162160	
8	-5.7804540	4.8804440	-0.0606460	
6	-6.0284970	6.0290820	-0.8522860	
1	-5.8533440	5.8214760	-1.9134500	
1	-5.4004630	6.8688710	-0.5355670	
1	-7.0770960	6.2795890	-0.6982200	
1	-1.4123440	4.6691380	-1.3514590	
1	-1.4991350	-4.6835160	-1.2521910	
1	0.5744830	4.3707730	-0.1982660	
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ACCEPTED MANUSCRIPT

1	0.4974810	-4.4044660	-0.0533070
9	7.0226010	3.7395990	-0.2030500
9	6.9700640	-3.7943040	-0.1783930

Compound 5 E= -1720.72334179 a.u.

	-		
5	-1.7906740	0.3791090	0.3377880
9	-2.7614470	0.6732920	-0.5869760
9	-2.2695680	0.4758930	1.6459610
7	-1.2218180	-1.0660150	0.1174950
6	0.1447270	-1.3346570	0.1180150
7	1.0795610	-0.4102030	0.1838640
6	0.7511150	0.8650830	0.2054450
7	-0.5583690	1.3357570	0.1828330
6	-1.8653500	-2.2394210	-0.0550650
6	-0.9171720	-3.2897250	-0.1592480
6	0.3483750	-2.7456120	-0.0439660
6	-0.5048250	2.6764920	0.0370110
6	0.8488920	3.0930430	-0.0352470
6	1.6529910	1.9743660	0.0895370
6	1.6341800	-3.4508080	-0.0592210
6	1.6859120	-4.7902490	0.3543350
1	0.7804270	-5.2756660	0.7066290
6	2.8868110	-5.4893040	0.3468610
1	2.9100180	-6.5231650	0.6765460
6	4.0581700	-4.8612980	-0.0737660
6	4.0178760	-3.5314720	-0.4883610
1	4.9251250	-3.0377400	-0.8229560
6	2.8178560	-2.8283890	-0.4852290
1	2.7912220	-1.7972320	-0.8175590
6	3.1148210	1.9021420	0.0635860
6	3.8115110	0.8493240	0.6786570
1	3.2614940	0.0687790	1.1909240
6	5.1993440	0.7982850	0.6407710
1	5.7514050	-0.0063330	1.1136390
6	5.8865280	1.8125610	-0.0096880
6	5.2347730	2.8728060	-0.6234690
1	5.8123520	3.6404250	-1.1259260
6	3.8475960	2.9089920	-0.5830390
1	3.3227700	3.7190440	-1.0799930
6	-3.3191810	-2.4184810	-0.1389590
6	-3.8136130	-3.4264920	-0.9807900
6	-5.1799420	-3.6589920	-1.0760200
1	-5.5494230	-4.4327490	-1.7411870

6	-6.0704500	-2.8968420	-0.3219010	
6	-5.5857820	-1.9022450	0.5253090	
1	-6.2750310	-1.3134750	1.1220700	
6	-4.2203540	-1.6590670	0.6196330	
1	-3.8501330	-0.8985230	1.2957020	
6	-1.6594090	3.5790270	-0.0227300	
6	-1.5637640	4.7255060	-0.8258720	
6	-2.6162380	5.6299450	-0.8919450	
1	-2.5346060	6.5061180	-1.5270150	
6	-3.7730740	5.4077910	-0.1469450	
6	-3.8704140	4.2768450	0.6615960	
1	-4.7655180	4.1057890	1.2509610	
6	-2.8241070	3.3640960	0.7267130	
1	-2.8982050	2.4977190	1.3724470	
1	-0.6695720	4.8907250	-1.4194080	
1	-3.1227500	-4.0097440	-1.5819810	
1	1.1670900	4.1238980	-0.1052250	
1	-1.1707670	-4.3310890	-0.3005900	
9	7.2267230	1.7676650	-0.0473140	
1	4.9969850	-5.4061470	-0.0783910	
1	-7.1381420	-3.0790170	-0.3929190	
1	-4.5951740	6.1149240	-0.1951140	

Compound 6 E= -1949.75869866 a.u.

5	-1.1062760	0.1520520	0.4435550
9	-2.1100610	0.4046320	-0.4604470
9	-1.5667080	0.2295880	1.7613570
7	-0.4839410	-1.2669410	0.2112740
6	0.8923930	-1.4759130	0.1660760
7	1.7886700	-0.5122390	0.2028400
6	1.4053200	0.7476600	0.2405760
7	0.0769190	1.1614490	0.2642420
6	-1.0843960	-2.4675360	0.0571510
6	-0.0926320	-3.4748260	-0.0800820
6	1.1505250	-2.8764080	-0.0059380
6	0.0653160	2.5058910	0.1258360
6	1.3988360	2.9789550	0.0118530
6	2.2531120	1.8953630	0.1010280
6	2.4645380	-3.5264100	-0.0636940
6	2.5861030	-4.8639480	0.3411950
1	1.7135170	-5.3884390	0.7194730
6	3.8142880	-5.5122570	0.2919540
1	3.8909000	-6.5455930	0.6153460

6	4.9445190	-4.8343320	-0.1621090
6	4.8351680	-3.5056370	-0.5676880
1	5.7099040	-2.9726410	-0.9277710
6	3.6073570	-2.8534570	-0.5229790
1	3.5270960	-1.8226180	-0.8476250
6	3.7155350	1.8874450	0.0263510
6	4.4785250	0.8653430	0.6137200
1	3.9806660	0.0592130	1.1396060
6	5.8654470	0.8766620	0.5302940
1	6.4680300	0.0960590	0.9813250
6	6.4851050	1.9224320	-0.1377440
6	5.7667880	2.9536320	-0.7257970
1	6.2926860	3.7476540	-1.2437910
6	4.3813200	2.9271320	-0.6401700
1	3.8045220	3.7136420	-1.1169280
6	-2.5258570	-2.7097760	0.0181850
6	-3.0034420	-3.7646880	-0.7696280
6	-4.3578740	-4.0685590	-0.8379560
1	-4.6895350	-4.8817200	-1.4718630
6	-5.2668930	-3.3128100	-0.0916490
6	-4.8015190	-2.2630710	0.7127350
1	-5.5239450	-1.6997470	1.2937080
6	-3.4542910	-1.9634240	0.7664710
1	-3.1116400	-1.1636450	1.4106550
8	-6.6025290	-3.5198850	-0.0779590
6	-7.1153230	-4.5715770	-0.8769880
1	-6.8940700	-4.4048350	-1.9367270
1	-6.7055110	-5.5386460	-0.5658660
1	-8.1936680	-4.5666010	-0.7246000
6	-1.1234900	3.3562280	0.1071450
6	-1.0920770	4.5311350	-0.6539180
6	-2.1750480	5.4012340	-0.6963880
1	-2.1182890	6.2921530	-1.3096690
6	-3.3198170	5.1050070	0.0494530
6	-3.3603040	3.9384390	0.8261360
1	-4.2538820	3.7368750	1.4071730
6	-2.2819750	3.0758910	0.8542680
1	-2.3222880	2.1913790	1.4775890
8	-4.4275710	5.8786390	0.0883350
6	-4.4261420	7.0719140	-0.6755470
1	-4.3069780	6.8563910	-1.7428380
1	-3.6292040	7.7483000	-0.3479010
1	-5.3946380	7.5396080	-0.5042030
1	-0.2137760	4.7596020	-1.2500760

ACCEPTED MANUSCRIPT

1	-2.3073300	-4.3449030	-1.3676060	
1	1.6725690	4.0226140	-0.0573450	
1	-0.3030730	-4.5270750	-0.2113840	
9	7.8244550	1.9381850	-0.2188570	
1	5.9047190	-5.3392380	-0.1993650	
Con	npound 8 E= -1850.513	390976 a.u.		
5	-0.9147740	0.0099800	0.4371810	
9	-1.9478460	0.0046140	-0.4693430	
9	-1.3832000	0.0405250	1.7540870	
7	-0.0040940	-1.2512460	0.2572740	
6	1.3848300	-1.1637900	0.2312380	
7	2.0549010	-0.0306410	0.1917220	
6	1.4125390	1.1181170	0.1577440	
7	0.0262220	1.2419120	0.2092020	
6	-0.3333710	-2.5546730	0.1183510	
6	0.8506060	-3.3296070	0.0013730	
6	1.9370890	-2.4794690	0.0893910	
6	-0.2721840	2.5513040	0.0587780	
6	0.9296930	3.2939000	-0.0831980	
6	1.9955670	2.4168930	-0.0158560	
6	3.3607050	-2.8185460	0.0127550	
6	3.7604980	-3.9789610	-0.6661280	
1	3.0114890	-4.5987380	-1.1504680	
6	5.1037850	-4.3251620	-0.7486940	
1	5.3965890	-5.2238420	-1.2824430	
6	6.0718720	-3.5153750	-0.1563730	
6	5.6859550	-2.3602870	0.5212120	
1	6.4339820	-1.7281980	0.9898440	
6	4.3420860	-2.0130740	0.6109350	
1	4.0460350	-1.1186390	1.1470030	
6	3.4261450	2.7357700	-0.0833530	
6	4.3744810	1.8057340	-0.5371680	
1	4.0511250	0.8192550	-0.8481900	
6	5.7217670	2.1472930	-0.5917110	
1	6.4430910	1.4174200	-0.9465390	
6	6.1454450	3.4163510	-0.2021970	
6	5.2105930	4.3481500	0.2462790	
1	5.5318330	5.3372170	0.5574400	
6	3.8638900	4.0104810	0.3057240	
1	3.1428130	4.7315670	0.6795310	
6	-1.6893150	-3.1004320	0.1001900	
6	-1.9359200	-4.2494130	-0.6612580	
6	-3.1939400	-4.8385340	-0.7054530	

1	-3.3490410	-5.7173970	-1.3191450
6	-4.2370710	-4.2799460	0.0390850
6	-4.0012840	-3.1372720	0.8165020
1	-4.8225560	-2.7300580	1.3965610
6	-2.7495010	-2.5543100	0.8463100
1	-2.5802980	-1.6854150	1.4699290
8	-5.4966050	-4.7694730	0.0757600
6	-5.7769740	-5.9269120	-0.6917040
1	-5.6082290	-5.7428730	-1.7582680
1	-5.1637580	-6.7739890	-0.3654400
1	-6.8290660	-6.1520330	-0.5228230
6	-1.6145510	3.1306930	0.0279670
6	-1.8300960	4.2711960	-0.7557510
6	-3.0726670	4.8908510	-0.8157040
1	-3.2033290	5.7614900	-1.4465840
6	-4.1322300	4.3727820	-0.0651470
6	-3.9276220	3.2395700	0.7343640
1	-4.7607900	2.8637240	1.3186580
6	-2.6909700	2.6259160	0.7799860
1	-2.5468250	1.7651240	1.4205270
8	-5.3793070	4.8940410	-0.0430490
6	-5.6282660	6.0423770	-0.8346530
1	-5.4592650	5.8331430	-1.8965190
1	-4.9962500	6.8808340	-0.5223020
1	-6.6753450	6.2960690	-0.6754170
1	-1.0184760	4.6694160	-1.3570830
1	-1.1357890	-4.6790990	-1.2564290
1	0.9744190	4.3662190	-0.2127350
1	0.8700870	-4.4081830	-0.0700000
1	7.1978960	3.6784880	-0.2471800
1	7.1215240	-3.7840830	-0.2226090

Compound 9 E= -2177.67866629 a.u.

5	-1.8822680	0.0262760	0.4515520
9	-2.9023820	0.0057230	-0.4690720
9	-2.3691160	0.0850420	1.7607230
7	-0.9738150	-1.2414000	0.3101760
6	0.4150280	-1.1594760	0.3076780
7	1.0907110	-0.0300580	0.2550570
6	0.4529420	1.1199680	0.1854110
7	-0.9329920	1.2497030	0.2120730
6	-1.3060250	-2.5464590	0.1896960
6	-0.1241720	-3.3280760	0.1096470

6	0.9645660	-2.4801190	0.2025840
6	-1.2241330	2.5573950	0.0301860
6	-0.0183020	3.2926440	-0.1079120
6	1.0437850	2.4130370	-0.0060030
6	2.3856250	-2.8230130	0.1614040
6	2.7997190	-4.0043510	-0.4706160
1	2.0628280	-4.6437770	-0.9472150
6	4.1387400	-4.3608590	-0.5257180
1	4.4339730	-5.2780210	-1.0273110
6	5.0983030	-3.5278140	0.0574070
6	4.7049070	-2.3481380	0.6934860
1	5.4625010	-1.7185210	1.1479820
6	3.3639710	-2.0026380	0.7479260
1	3.0665440	-1.0907430	1.2524410
6	2.4739370	2.7235720	-0.0566800
6	3.4343280	1.7752690	-0.4479660
1	3.1198520	0.7763910	-0.7257900
6	4.7801370	2.1039430	-0.4873030
1	5.5228640	1.3741380	-0.7921460
6	5.1983030	3.3905920	-0.1411700
6	4.2575250	4.3492770	0.2459980
1	4.5709680	5.3515390	0.5238560
6	2.9132410	4.0109010	0.2852910
1	2.1922390	4.7545300	0.6109550
6	-2.6638250	-3.0865180	0.1577090
6	-2.9027000	-4.2486540	-0.5860130
6	-4.1625610	-4.8328040	-0.6407680
1	-4.3114850	-5.7222350	-1.2405880
6	-5.2155810	-4.2555720	0.0751400
6	-4.9877890	-3.0992060	0.8346130
1	-5.8169520	-2.6774120	1.3925680
6	-3.7339960	-2.5213650	0.8748660
1	-3.5712280	-1.6414670	1.4846490
8	-6.4776170	-4.7388850	0.0996480
6	-6.7499290	-5.9107370	-0.6487600
1	-6.5624650	-5.7491460	-1.7158000
1	-6.1458140	-6.7532590	-0.2948780
1	-7.8056480	-6.1282390	-0.4931570
6	-2.5637530	3.1403000	-0.0337170
6	-2.7633670	4.2655910	-0.8432690
6	-4.0025910	4.8880930	-0.9341960
1	-4.1207080	5.7462500	-1.5843700
6	-5.0751710	4.3887150	-0.1893790
6	-4.8867520	3.2708130	0.6353360

1	-5.7299630	2.9095540	1.2143750
6	-3.6532040	2.6541010	0.7117790
1	-3.5219410	1.8058440	1.3715030
8	-6.3202920	4.9146260	-0.1960540
6	-6.5529220	6.0492910	-1.0120750
1	-6.3691260	5.8200590	-2.0673010
1	-5.9221970	6.8908800	-0.7056140
1	-7.6012030	6.3097440	-0.8730090
1	-1.9414840	4.6490030	-1.4402800
1	-2.0945790	-4.6930660	-1.1591610
1	0.0313260	4.3619040	-0.2589490
1	-0.1087220	-4.4079460	0.0606120
7	6.5935850	3.6323920	-0.2118740
7	6.4898880	-3.7977810	0.0533500
7	6.8433560	-4.8430990	-0.5062600
7	6.9676950	4.7722210	0.0903550
7	7.2731860	-5.7673270	-0.9890610
7	7.4153580	5.7758610	0.3444120

Compound 10 E= -2005.11678847 a.u.

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5	-1.3069270	0.0239550	0.4386450
9	-2.3368660	0.0427130	-0.4725540
9	-1.7841970	0.0596430	1.7536190
7	-0.4192180	-1.2501210	0.2594150
6	0.9684350	-1.1885520	0.2454300
7	1.6628550	-0.0616120	0.2115640
6	1.0439340	1.0930360	0.1767420
7	-0.3432010	1.2399330	0.2217540
6	-0.7725080	-2.5501500	0.1177850
6	0.3948660	-3.3429610	0.0117670
6	1.4974020	-2.5077260	0.1087080
6	-0.6160250	2.5549600	0.0774330
6	0.5960890	3.2806560	-0.0540940
6	1.6524970	2.3904140	0.0126590
6	2.9154530	-2.8694820	0.0455720
6	3.3086570	-4.0272790	-0.6419020
1	2.5591740	-4.6321040	-1.1431610
6	4.6446390	-4.3994580	-0.7165660
1	4.9614020	-5.2883760	-1.2504220
6	5.5905300	-3.5961490	-0.0964270
6	5.2435330	-2.4445760	0.5944250
1	6.0157900	-1.8520600	1.0725330
6	3.9024670	-2.0876390	0.6669970

1	3.6145140	-1.1967540	1.2129850	
6	3.0790360	2.6888110	-0.0470350	
6	4.0420150	1.7283940	-0.4053240	
1	3.7261360	0.7213360	-0.6514400	
6	5.3872840	2.0503070	-0.4622080	
1	6.1122560	1.2923780	-0.7476540	
6	5.8306050	3.3495060	-0.1630030	
6	4.8738180	4.3151580	0.1948540	
1	5.1984750	5.3222890	0.4410640	
6	3.5315130	3.9864150	0.2471830	
1	2.8161620	4.7471190	0.5464150	
6	-2.1409570	-3.0685450	0.0893980	
6	-2.4100500	-4.2026830	-0.6855170	
6	-3.6791530	-4.7687040	-0.7349050	
1	-3.8505220	-5.6377230	-1.3583570	
6	-4.7114170	-4.1995830	0.0158930	
6	-4.4540670	-3.0700770	0.8047700	
1	-5.2675610	-2.6530310	1.3889240	
6	-3.1906780	-2.5117070	0.8414260	
1	-3.0052080	-1.6521770	1.4734850	
8	-5.9811500	-4.6665750	0.0479160	
6	-6.2812080	-5.8103210	-0.7314680	
1	-6.1095910	-5.6183540	-1.7962980	
1	-5.6825150	-6.6715450	-0.4149750	
1	-7.3370080	-6.0197180	-0.5648980	
6	-1.9482110	3.1568410	0.0393460	
6	-2.1380420	4.3051590	-0.7397520	
6	-3.3697290	4.9451420	-0.8073930	
1	-3.4808570	5.8208800	-1.4349380	
6	-4.4439100	4.4406320	-0.0683080	
6	-4.2648020	3.3001180	0.7270490	
1	-5.1090170	2.9351400	1.3022620	
6	-3.0391750	2.6654580	0.7792670	
1	-2.9146880	1.7987090	1.4157710	
8	-5.6821980	4.9820780	-0.0540960	
6	-5.9061710	6.1377540	-0.8425910	
1	-5.7314970	5.9304280	-1.9038920	
1	-5.2636150	6.9646320	-0.5210750	
1	-6.9504050	6.4073120	-0.6910050	
1	-1.3149020	4.6929650	-1.3320530	
1	-1.6178200	-4.6399240	-1.2859160	
1	0.6524410	4.3530230	-0.1762190	
1	0.3979290	-4.4220130	-0.0577070	
9	6.8848790	-3.9462800	-0.1669760	

7	7.1785570	3.6573280	-0.1630720	
1	7.4072440	4.6361280	-0.2795330	
1	7.7677710	3.0552490	-0.7233960	

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- Aymmetric/asymmetric fluorine-containing aza-BODIPYs at 1/7-positions were prepared.
- The effect of the withdrawing -F group at 1/7-position on the photophysical properties is found to be almost negligible.
- The replacement of -F atoms with $-N_3/-NH_2$ groups resulted in a remarkable bathochromic shift.
- Aza-BODIPY with a -NH₂ group could be used as a turn-on fluorescent probe for pH value.

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