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**A selective colorimetric and fluorometric ammonium ion  
sensor based on the H-aggregation of an aza-BODIPY with  
fused pyrazine rings**

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## I. Experimental details

### I.1 Materials and methods

All reagents were obtained from commercial suppliers and used as supplied unless otherwise indicated. Air and moisture-sensitive reactions were carried out under an argon atmosphere.  $\text{CH}_2\text{Cl}_2$  and diethyl ether were distilled over calcium hydride and sodium, respectively. Triethylamine was obtained by simple distillation. NMR spectra were measured with a Bruker DRX500 spectrometer and referenced to the residual proton signals of the solvent. Mass spectra were measured with a Bruker Daltonics Autoflex<sup>III</sup> MALDI TOF spectrometer. Fluorescence spectra were measured on an Edinburgh LFS-920 fluorescence spectrophotometer.

### I.2 X-Ray structure determination

The X-ray diffraction data were collected on a Bruker Smart Apex CCD diffractometer with graphite monochromated Mo  $K\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) using the  $\omega$ - $2\theta$  scan mode. The data were corrected for Lorentz and polarization effects. The structure was solved by direct methods and refined on  $F^2$  by full-matrix least-squares methods using SHELXTL-2000 and all molecular graphics are derived from the SHELX-2000 program package.<sup>S1</sup> A red-pink block-like aza-BODIPY crystal with approximate  $1 \times 0.3 \times 0.1 \text{ mm}^3$  dimensions was measured. Orthorhombic, space group  $Pbcn$ ,  $a = 19.167(5) \text{ \AA}$ ,  $b = 12.636(3) \text{ \AA}$ ,  $c = 11.550(3) \text{ \AA}$ ,  $V = 2797.4(13) \text{ \AA}^3$ ,  $Z = 4$ ,  $F(000) = 1176.0$ ,  $\rho = 1.333 \text{ g cm}^{-3}$ ,  $2\theta_{\text{max}} = 56.74^\circ$ ,  $R_1 = 0.0592$ ,  $wR_2 = 0.1695$ ,  $\text{GOF} = 1.028$ , residual electron density between 0.51 and  $-0.26 \text{ e\AA}^{-3}$ . CCDC-843443 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/conts/retrieving.html](http://www.ccdc.cam.ac.uk/conts/retrieving.html) (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

### I.3 Synthesis section

5,6-Diethylpyrazine-2,3-dicarbonitrile (**1**) was synthesized according to literature methods.<sup>S2</sup> A mixture of 3,4-hexanedione (11.4 g, 0.1 mol) and diaminomaleonitrile (21.6 g, 0.2 mol) in water (120 ml), ethanol (180 ml) and acetic acid (8 ml) were heated at reflux for *ca.* 1 hour, cooled, filtered, and recrystallized from a mixed solution of 10 ml ethanol and 200 ml water to give colorless needle-shaped products. Further purification was carried out by elution on a silica column with  $\text{CH}_2\text{Cl}_2$ . Yield: 60%. MALDI-TOF: Anal. Calcd. 211.1 ( $\text{C}_{10}\text{H}_{10}\text{N}_4\text{Na}$ : [ $M^+$ +Na]). Found 211.4. IR (KBr,  $\text{cm}^{-1}$ ): 3416b, 2985m, 2242m, 2170w, 1638s, 1535m, 1460w, 1401vs, 1308m, 1165m, 782s, 619w, 776w, 435w.

(Z)-N-(2,3-diethyl-7-phenyl-5H-pyrrolo[3,4-*b*]pyrazin-5-ylidene)-2,3-diethyl-7-phenyl-6H-pyrrolo[3,4-*b*]pyrazin-5-amine (**2**). An aryl Grignard compound (1.1 eq.) in diethyl ether (20 ml) was added to a suspension of the appropriate phthalodinitrile (1.86g, 10 mmol) in dry diethyl ether (20ml) at  $-20^\circ\text{C}$  under argon. The reaction mixture was stirred at room temperature for 4 hours. The reaction mixture was rotated to dryness under vacuum and then refluxed with formamide until the color changed from yellow to blue and purple. After isolation by silica column, the blue fraction was collected. Yield: 10%. MALDI-TOF: Anal. Calcd. 514.3 ( $\text{C}_{32}\text{H}_{32}\text{N}_7$ : [ $M^+$ +H]). Found 514.4.

2,3,7,8-tetraethyl-12,12-difluoro-10,14-diphenyl-12H-pyrazino[2',3':3,4]pyrrolo[1,2-*c*]pyrazino[2',3':3,4]pyrrolo[2,1-*f*][1,3,5,2]triazaborinin-11-ium-12-uide (**3**). Compound **2** (1mmol) was dissolved in  $\text{CH}_2\text{Cl}_2$  (50 ml) and diisopropylethylamine (or tri-ethylamine, 3 ml) was added. The mixture was stirred for 0.5 to 1 hour and  $\text{BF}_3 \cdot \text{OEt}_2$  (5 ml) was added at room temperature. The mixture was then heated at reflux until complete conversion of the starting material was observed after about 3 hours (monitored by thin layer chromatography). After cooling the reaction mixture was quenched and washed 3 times with water (50 ml each time) and extracted with chloroform. The combined organic layers were dried with anhydrous  $\text{Na}_2\text{SO}_4$  and then concentrated *in vacuo*. The crude product was purified on a silica gel column by elution with  $\text{CH}_2\text{Cl}_2$ . Yield: 60%. Anal. HR-MS: Calcd. for ( $\text{C}_{32}\text{H}_{31}\text{BF}_2\text{N}_7$ : [ $M^+$ +H]) 562.27. Found 562.29 in FT-MS ESI SIM MS spectrum. NMR:  $\delta = 8.36$  (d,  $J = 5 \text{ Hz}$ , 2 H), 8.34 (d,  $J = 5 \text{ Hz}$ , 2 H), 7.58 (t,  $J = 5 \text{ Hz}$ , 6H), 3.13 (q,  $J = 10 \text{ Hz}$ , 4 H), 3.04 (q,  $J = 10 \text{ Hz}$ , 4 H), 1.48 (t,  $J = 10 \text{ Hz}$ , 6 H), 1.41 (t,  $J = 10 \text{ Hz}$ , 6H).

### I.4 TD-DFT calculations

The Gaussian 03W software package<sup>S3</sup> was used to carry out gas phase density functional theory (DFT) geometry optimizations. The hybrid B3LYP functional was selected and either 6-31G(d) or 3-21G basis sets were used. The same approach was used to obtain excitation energies and oscillator strengths from time-dependent density functional theory (TD-DFT) calculations.



II.2

liuhanzhuang #1-103 RT: 0.01-2.86 AV: 103 NL: 8.55E4  
T: FTMS + p ESI SIM ms [557.44-567.44]

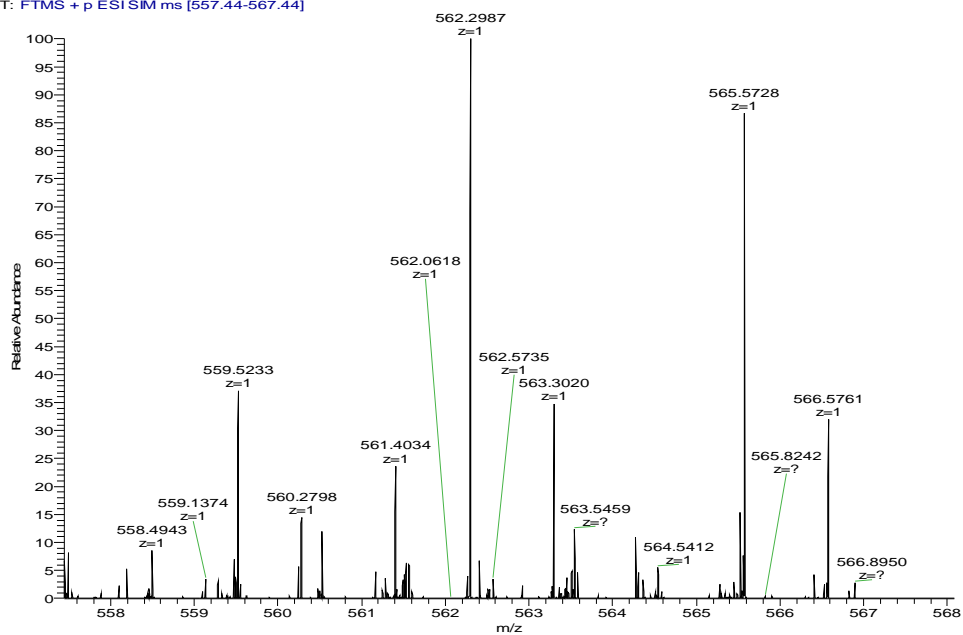
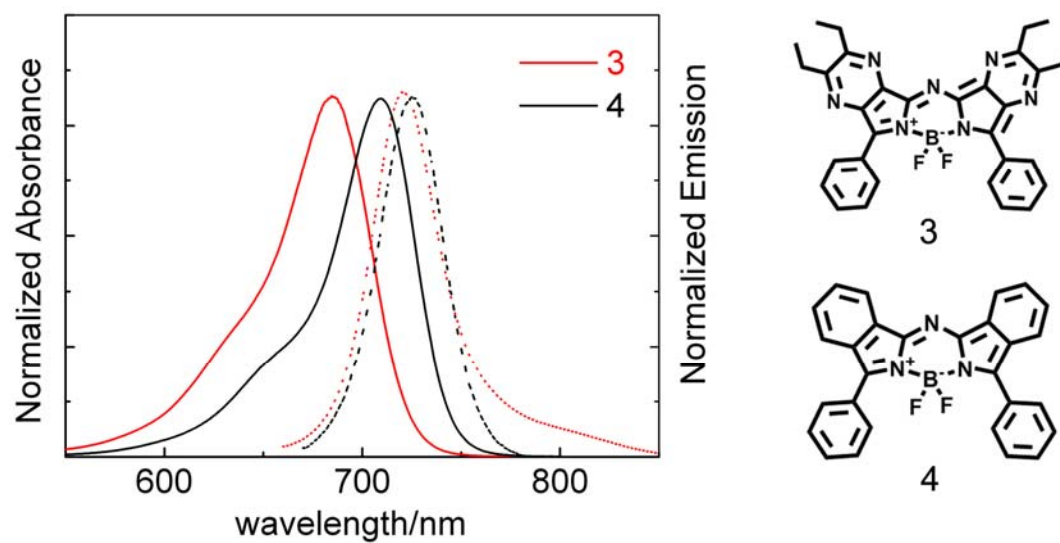


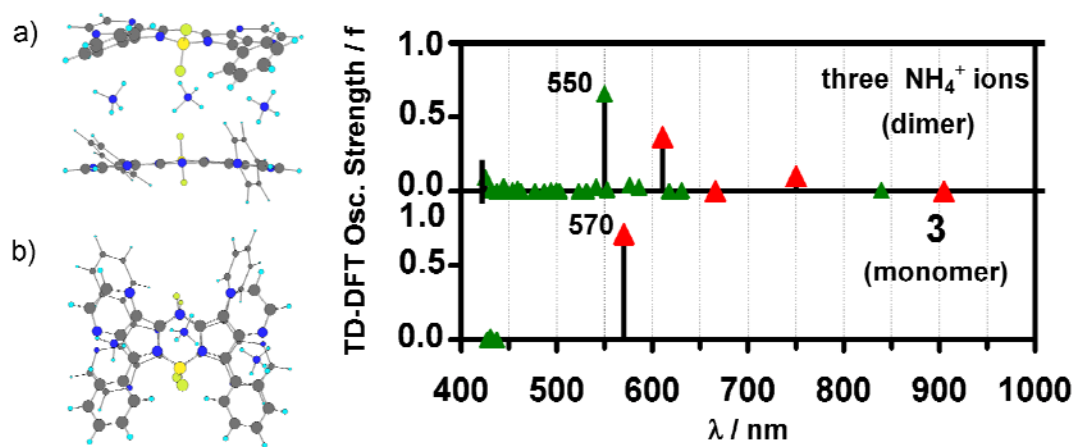
Figure S2. HR-MS spectrum of 3.

II.3



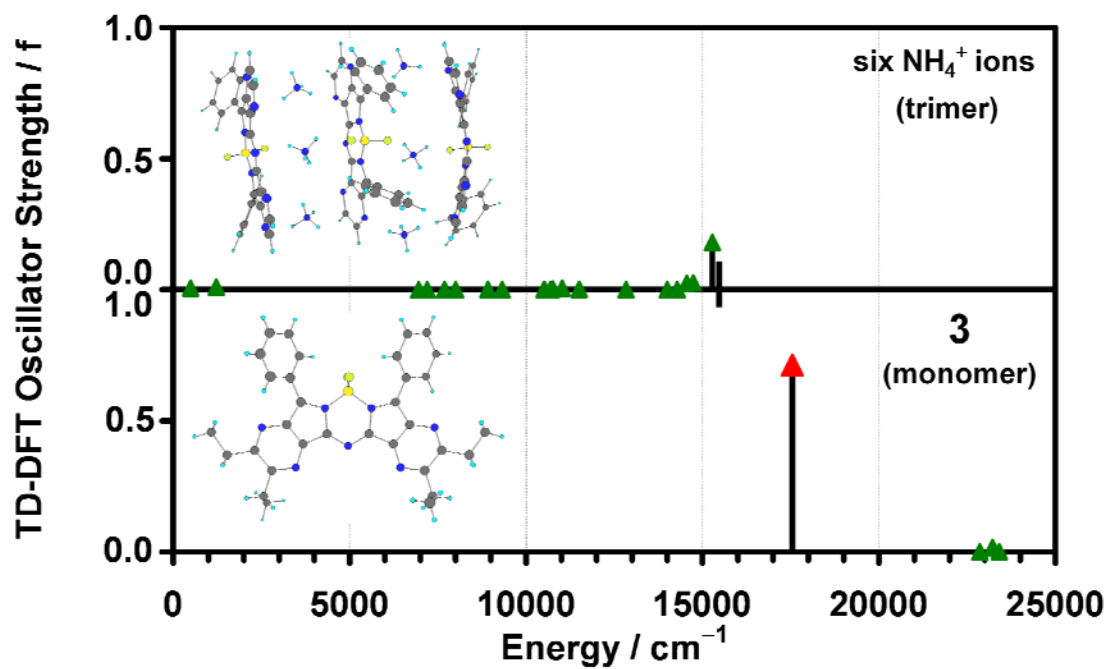
**Figure S3.** Absorption (solid lines) and fluorescence (dotted lines) spectra of **3** and **4** in THF.

II.4



**Figure S4.** B3LYP geometry optimization for a dimer complex with three NH<sub>4</sub><sup>+</sup> ions viewed from a) the side (top left) and b) from above (bottom left). TD-DFT spectra of **3** and the model dimer structure based on geometry calculations (right) carried out using the B3LYP functional with 6-31G(d) and 3-21G basis sets, respectively. Transitions associated with the HOMO → LUMO transition of the monomer are highlighted with red diamonds. Although a low lying forbidden band is predicted for the model dimer, the calculation is complicated in the region of the main H-aggregate band by configuration interaction with higher energy  $\pi\pi^*$  states. A gas phase calculation is unlikely to provide accurate results in this context, since solvation effects and the influence of counter ions are not taken into consideration.

II.5



**Figure S5.** Calculated TD-DFT spectra for the X-ray structure of **3**, using 6-31G(d) basis sets, and a model aggregated trimer complex with a face-to-face arrangement of the monomer units aligned at 180° to its next nearest neighbor coordinated by six NH<sub>4</sub><sup>+</sup> ions, using 3-21G basis sets. The HOMO-LUMO transition of the monomer is highlighted with a red diamond.

II.6

Table S1. Crystal data and structure refinement for **3**.

	<b>3</b>	Max. and min. transmission	0.991 and 0.913
Empirical formula	C <sub>32</sub> H <sub>30</sub> BF <sub>2</sub> N <sub>7</sub>	θ range for data collection (°)	1.93 to 28.37
Formula weight	561.26	Index ranges	-25 ≤ h ≤ 25, -16 ≤ k ≤ 12, -15 ≤ l ≤ 14
Crystal size (mm <sup>3</sup> )	1 × 0.3 × 0.1	Total reflections	16633
Crystal system	Orthorhombic	Independent reflections	3474 [R <sub>(int)</sub> = 0.1167]
Space group	Pbcn	Parameters	197
Z	4	Final R indices [I > 2σ <sub>(I)</sub> ]	R <sub>1</sub> = 0.0592 wR <sub>2</sub> = 0.1534
a / Å	19.167(5)	R indices (all data)	R <sub>1</sub> = 0.1057 wR <sub>2</sub> = 0.1695
b / Å	12.636(3)	Goodness-of-fit on F <sup>2</sup>	1.028
c / Å	11.550(3)	Largest diff. peak and hole (eÅ <sup>-3</sup> )	0.511 and -0.261
α / (deg)	90	Max. and min. transmission	0.991 and 0.913
β / (deg)	90	θ range for data collection (°)	1.93 to 28.37
γ / (deg)	90	Index ranges	-25 ≤ h ≤ 25, -16 ≤ k ≤ 12, -15 ≤ l ≤ 14
Volume / Å <sup>3</sup>	90	Total reflections	16633
Density (calc.) Mg/m <sup>3</sup>	1.333	Independent reflections	3474 [R <sub>(int)</sub> = 0.1167]
Absorption coefficient (mm <sup>-1</sup> )	0.091	Parameters	197
Temperature (K)	296(2)	Final R indices [I > 2σ <sub>(I)</sub> ]	R <sub>1</sub> = 0.0592 wR <sub>2</sub> = 0.1534
F(000)	1176	R indices (all data)	R <sub>1</sub> = 0.1057 wR <sub>2</sub> = 0.1695
Goodness-of-fit on F <sup>2</sup>	1.028	Largest diff. peak and hole (eÅ <sup>-3</sup> )	0.511 and -0.261



### III. References

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