A New *N*-imidazolyl-1,8-naphthalimide Based Fluorescent Sensor for Fluoride Detection

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General

Absorbance spectra are collected by 8453 UV-Visible Spectrophotometer (Agilent Technologies). Fluorescence measurements are carried out in а RF-5301 Spectrofluorophotometer (Shimadzu, Japan). The fluorescence spectra are recorded in a 1 cm quartz cuvette at room temperature. The excitation and emission slits are set at 5 nm. ¹H and ¹³C NMR spectra were recorded on Bruker 300 UltraShield. All reagents are purchased from Sigma-Aldrich (MO, USA), Fisher Scientific (USA) and Acros Organics (USA) in analytical grade and used as received, unless otherwise stated.

Synthesis



6-bromo-2-cyclopentyl-1H-benzo[de]isoquinoline-1,3(2H)-dione (1a) A mixture of 4-bromo-1,8-naphthalic anhydride (0.276g, 1mmol) and cyclopentanamine (0.170g, 2 mmol) in 5.0 mL pyridine was refluxed for 12 hr under argon atmosphere¹. After the reaction, mixture was cooled down to room temperature, pyridine was removed by rotary evaporation to give the crude product that was purified by column chromatography (silica, 220-400 mesh, CH₂Cl₂ : Hexane = 1: 1 ν/ν). The product is isolated as a white solid **1a** (0.267g, 78%). ¹H NMR (300 MHz, CDCl₃) δ : 1.72 (m, 2H), 2.05(m, 6H), 5.56 (m, 1H), 7.80(t, *J*=8.1Hz, 1H), 7.97 (d, *J*=8.1Hz, 1H), 8.35 (d, *J*=8.1Hz, 1H), 8.46 (d, *J*=7.8Hz, 1H), 8.60 (d, *J*=6.3Hz, 1H); ¹³C (75MHz, CDCl₃) δ : 26.1, 28.8, 52.8, 122.7, 123.6, 128.1, 128.8, 129.8, 130.4, 131.1, 131.1, 131.9, 132.9, 163.9. MS: m/z

 $(M^{\scriptscriptstyle +})$ 343.02. Anal. Calcd. for $C_{17}H_{14}BrNO_2$: C, 59.32; H, 4.10; N, 4.07. Found: C, 59.18; H, 4.06, N, 4.19.

6-bromo-2-(2-hydroxyphenyl)-1H-benzo[de]isoquinoline-1,3(2H)-dione (1b) 4-bromo-1,8-naphthalic anhydride (0.276g, 1mmol) and 2-aminophenol (0.218g, 2 mmol) in 5.0 mL pyridine were refluxed for 12 hr under argon atmosphere. After the reaction, mixture was cooled down to room temperature, pyridine was removed by rotary evaporation to give the crude product that was purified by column chromatography (silica, 220-400 mesh, CH₂Cl₂ : EtOAc = 4: 1 ν/ν). The product is isolated as an orange solid **1b** (0.198g, 54%). ¹H NMR (300 MHz, DMSO) δ : 6.96 (m, 2H), 7.27 (m, 2H), 8.05 (t, *J*=6.9 Hz, 1H), 8.26(d, *J*=8.2Hz, 1H), 8.32 (d, *J*=8.4Hz, 1H), 8.61 (m, 2H), 9.63 (s, 1H); ¹³C (75MHz, DMSO) δ : 117.0, 119.6, 123.1, 123.1, 123.9, 129.3, 129.4, 129.6, 130.2, 130.4, 130.7, 131.4, 131.9, 132.1, 133.2, 153.8, 163.3. MS: *m/z* (M⁺) 366.98. Anal. Calcd. for C₁₈H₁₀BrNO₃: C, 58.72; H, 2.74; N, 3.80. Found: C, 58.69; H, 2.67; N, 3.91.

6-bromo-2-(1H-imidazol-2-yl)-1H-benzo[de]isoquinoline-1,3(2H)-dione (1c) A mixture of 4bromo-1,8-naphthalic anhydride (0.276g, 1mmol) and 2-aminoimidazole sulfate (0.215g, 1 mmol) in 5.0 mL pyridine was refluxed for 12 hr under argon atmosphere. After the reaction, mixture was cooled down to room temperature, pyridine was removed by rotary evaporation to give the crude product that was purified by column chromatography (silica, 220-400 mesh, CH₂Cl₂ : EtOAc = 1: 4 *v/v*). The product is isolated as a yellow solid **1c** (0.092g, 27%). ¹H NMR (300 MHz, DMSO) δ: 7.09 (s, 1H), 7.28 (s, 1H), 8.16 (t, *J*=7.0 Hz, 1H), 8.27(d, *J*=7.8Hz, 1H), 8.43 (d, *J*=7.2Hz, 1H), 8.70 (m, 2H), 12.20 (s, 1H); ¹³C (75MHz, DMSO) δ: 116.1, 117.2, 121.4, 128.7, 129.6, 130.7, 132.1, 132.2, 132.7, 133.1, 134.1, 137.0, 160.9, 161.8, 162.5. MS: *m/z* (M⁺) 340.98. Anal. Calcd. for C₁₅H₈BrN₃O₂: C, 52.66; H, 2.36; N, 12.28. Found: C, 52.42; H, 2.49; N, 12.31.

3-amino-1,8-naphthalimide 3-nitro-1,8-naphthalic anhydride (1.0g) was mixed with tin(II) chloride (7.0g) in conc. hydrochloric acid (7.0 ml) and refluxed for 2 hr. The reaction mixture was cooled and filtered to give yellow solid². The crude product was recrystallized in glacial acetic acid to yield product as yellow solid (0.789g, 90%). ¹H NMR (300 MHz, DMSO) δ : 7.35 (s, 1H), 7.65 (t, *J*=7.2 Hz, 1H), 7.96 (s, 1H), 8.10(m, 2H); ¹³C (75MHz, DMSO) δ : 113.1, 119.0, 119.7, 123.3, 123.5, 127.7, 127.8, 133.0, 134.1, 148.6, 161.4, 161.5. MS: *m/z* (M⁺) 213.16

5-amino-2-cyclopentyl-1H-benzo[de]isoquinoline-1,3(2H)-dione (2a) A mixture of 3-amino-1,8-naphthalic anhydride (0.213g, 1mmol) and cyclopentanamine (0.170g, 2 mmol) in 5.0 mL pyridine was refluxed for 12 hr under argon atmosphere¹. After the reaction, mixture was cooled down to room temperature, pyridine was removed by rotary evaporation to give the crude product that was purified by column chromatography (silica, 220-400 mesh, CH₂Cl₂ : ethyl acetate = 11: 1 ν/ν). The product is isolated as a yellow solid **2a** (0.176g, 63%). ¹H NMR (300 MHz, CDCl₃) δ : 1.65(m, 3H), 2.09(m, 5H), 4.17(s, 2H), 5.60(m, 1H), 7.32 (s, 1H), 7.64 (t, *J*=7.5Hz, 1H), 7.99 (m, 2H), 8.35 (d, *J*=6.3Hz, 1H); ¹³C (75MHz, CDCl₃) δ : 26.1, 28.8, 52.3, 114.1, 122.1, 124.2, 127.3, 131.2, 133.6, 145.1, 164.6. MS: m/z (M⁺) 280.07. Anal. Calcd. for C₁₇H₁₆N₂O₂: C, 72.84; H, 5.75; N, 9.99. Found: C, 73.01; H, 5.56, N, 9.91.

5-amino-2-(2-hydroxyphenyl)-1H-benzo[de]isoquinoline-1,3(2H)-dione (2b) A mixture of 3-amino-1,8-naphthalic anhydride (0.213g, 1mmol) and 2-aminophenol (0.218g, 2 mmol) in 5.0

mL pyridine was refluxed for 12 hr under argon atmosphere. After the reaction, mixture was cooled down to room temperature, pyridine was removed by rotary evaporation to give the crude product that was purified by column chromatography (silica, 220-400 mesh, CH₂Cl₂ : EtOAc = 2: 1 v/v). The product is isolated as a yellow solid **2b** (0.170g, 56%). ¹H NMR (300 MHz, acetone-d6) δ : 5.44(s, 2H), 7.02(m, 2H), 7.30 (m, 2H), 7.45(s, 1H), 7.66(t, *J*=6.6 Hz, 1H), 8.07 (m, 2H), 8.18(d, *J*=8.1Hz, 1H), 8.58 (s,1H); ¹³C (75MHz, acetone-d6) δ : 112.3, 116.5, 119.6, 121.7, 122.1, 123.2, 123.7, 124.1, 125.7, 126.8, 129.5, 130.4, 131.4, 134.1, 147.6, 153.7, 163.6, 163.9. MS: m/z (M⁺) 304.10. Anal. Calcd. for C₁₈H₁₂N₂O₃: C, 71.05; H, 3.97; N, 9.21. Found: C, 70.84; H, 3.91; N, 9.30.

5-amino-2-(1H-imidazol-2-yl)-1H-benzo[de]isoquinoline-1,3(2H)-dione (2c) A mixture of 3-amino-1,8-naphthalic anhydride (0.213g, 1mmol) and 2-aminoimidazole sulfate (0.215g, 1 mmol) in 5.0 mL pyridine was refluxed for 12 hr under argon atmosphere. After the reaction, mixture was cooled down to room temperature, pyridine was removed by rotary evaporation to give the crude product that was purified by column chromatography (silica, 220-400 mesh, MeOH : EtOAc = 1: 5 *v/v*). The product is isolated as a yellow solid **2c** (0.086g, 31%). ¹H NMR (300 MHz, DMSO) δ : 6.10 (s, 2H), 7.02 (m, 1H), 7.27 (m, 1H), 7.37(s, 1H), 7.68 (t, *J*=7.4Hz, 1H), 8.02 (s, 1H), 8.13(m, 2H), 12.23 (s, 1H); ¹³C (75MHz, DMSO) δ : 113.1, 121.4, 121.6, 122.4, 126.3, 127.8, 132.9, 134.1, 148.6. MS: *m/z* (M⁺) 278.07. Anal. Calcd. for C₁₅H₁₀N₄O₂: C, 64.74; H, 3.62; N, 20.13. Found: C, 64.49; H, 3.76; N, 20.25.

2-cyclopentyl-1H-benzo[de]isoquinoline-1,3(2H)-dione (3a)) A mixture of 1,8-naphthalic anhydride (0.198g, 1mmol) and cyclopentanamine (0.170g, 2 mmol) in 5.0 mL pyridine was refluxed for 12 hr under argon atmosphere¹. After the reaction, mixture was cooled down to room temperature, pyridine was removed by rotary evaporation to give the crude product that was purified by column chromatography (silica, 220-400 mesh, CH₂Cl₂ : Hexane = 1: 10 ν/ν). The product is isolated as a light brown solid **3a** (0.215g, 81%). ¹H NMR (300 MHz, CDCl₃) δ : 1.69 (m, 2H), 2.13(m, 6H), 5.61 (m, 1H), 7.79(t, *J*=8.2Hz, 2H), 8.21 (d, *J*=7.9Hz, 2H), 8.62 (d, *J*=7.8Hz, 2H); ¹³C (75MHz, CDCl₃) δ : 26.1, 28.8, 52.7, 123.2, 126.9, 127.5, 131.1, 131.5, 133.6, 164.6. MS: m/z (M⁺) 265.11. Anal. Calcd. for C₁₇H₁₅NO₂: C, 76.96; H, 5.70; N, 5.28. Found: C, 76.88; H, 5.51, N, 5.39.

2-(2-hydroxyphenyl)-1H-benzo[de]isoquinoline-1,3(2H)-dione (3b) A mixture of 1,8-naphthalic anhydride (0.198g, 1mmol) and 2-aminophenol (0.218g, 2 mmol) in 5.0 mL pyridine was refluxed for 12 hr under argon atmosphere. After the reaction, mixture was cooled down to room temperature, pyridine was removed by rotary evaporation to give the crude product that was purified by column chromatography (silica, 220-400 mesh, CH₂Cl₂ : EtOAc = 2: 1 ν/ν). The product is isolated as a light yellow solid **3b** (0.240g, 83%). ¹H NMR (300 MHz, DMSO) δ : 6.96(m, 2H), 7.26 (m, 2H), 7.90 (m, 2H), 8.56 (m, 4H), 9.65(s, 1H); ¹³C (75MHz, DMSO) δ : 116.9, 119.5, 123.1, 123.4, 127.7, 128.5, 130.2, 130.6, 131.1, 131.9, 134.8, 153.9, 163.9. MS: m/z (M⁺) 289.15. Anal. Calcd. for C₁₈H₁₁NO₃: C, 74.73; H, 3.83; N, 4.84. Found: C, 74.59; H, 3.69; N, 4.84.

2-(1H-imidazol-2-yl)-1H-benzo[de]isoquinoline-1,3(2H)-dione (3c) A mixture of 1,8-naphthalic anhydride (0.198g, 1mmol) and 2-aminoimidazole sulfate (0.215g, 1 mmol) in 5.0 mL pyridine was refluxed for 12 hr under argon atmosphere. After the reaction, mixture was cooled

down to room temperature, pyridine was removed by rotary evaporation to give the crude product that was purified by column chromatography (silica, 220-400 mesh, CH_2Cl_2 : EtOAc = 1: 1 ν/ν). The product is isolated as a brown solid **3c** (0.110g, 42%). ¹H NMR (300 MHz, DMSO) δ : 7.24 (m, 2H), 7.91 (m, 2H), 8.61 (m, 4H), 11.74(s, 1H); ¹³C (75MHz, DMSO) δ : 114.9, 120.8, 122.1, 129.3, 131.4, 133.1, 134.2, 137.1, 162.5, 165.4. MS: m/z (M⁺) 263.11. Anal. Calcd. for C₁₅H₉N₃O₂: C, 68.44; H, 3.45; N, 15.96. Found: C, 68.49; H, 3.39; N, 15.78.

Reference

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Fig. S1 Fluorescence emission spectra change of **1a**, **2a**, **3a**, **1b**, **2b**, and **3b** $(5.0 \times 10^{-6} \text{M})$ in the presence of 10 equiv. F⁻ (TABF) in CH₂Cl₂ at room temperature.



Fig. S2 No significant change were observed for absorption spectra of **1a**, **2a**, **3a**, **1b**, **2b**, and **3b** (1.0×10^{-3} M) in the presence of 1 equiv. F⁻ (TABF) in CH₂Cl₂ at room temperature.



Fig. S3 1c, 2c and 3c showed solvation effect in different solvents (dichloromethane, acetonitrile and methanol) at room temperature.



Fig. S4 The competition experiment of **1c** (5.0×10^{-6} M) in CH₂Cl₂ upon addition of 1 equiv one of anions (Cl⁻, Br⁻, I⁻, NO₃⁻, OAc⁻, H₂PO₄⁻ or HSO₄⁻) and 1 equiv F⁻ (λ_{ex} =344 nm, λ_{em} =442 nm).



Fig. S5 1c (5.0×10^{-6} M) showed 1:1 stoichiometry with F⁻ in CH₂Cl₂⁻ (λ_{ex} =344 nm, λ_{em} =442 nm).

	Cl	Br⁻	I_	NO ₃ ⁻	OAc	H ₂ PO ₄ ⁻	HSO ₄
Log K _a	2.41±0.14	2.01±0.09	1.89±0.12	1.10±0.17	3.08±0.21	3.46±0.19	1.78±0.08

Table S1 The binding constants of anions with **1c** $(5.0 \times 10^{-6} \text{M})$ in CH₂Cl₂ at room temperature.





























DMSO-dB



















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