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Supporting Information

Unusual Blue-Shifted Acid-Responsive Photoluminescence Behavior in 6-Amino-8-cyanobenzo[1,2-*b*]indolizines

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1 Experimental Procedures

1.1 General Information

Reactions requiring anhydrous conditions were conducted under an inert atmosphere of argon using anhydrous solvents. DCM and toluene were distilled over CaH₂. Et₂O and THF were distilled over Na and benzophenone. All reactions were monitored by analytical thin-layer chromatography (TLC) using indicated solvent systems on Analtech Uniplate Silica Gel TLC plates (250 microns). All NMR spectra were recorded on either Bruker Avance 400 MHz or 300 MHz spectrometers as indicated. Chemical shifts (δ) are quoted in parts per million (ppm) and referenced to the following residual solvent signals: 1H δ = 7.26 (CDCl₃), 2.50 (DMSO-d₆), 3.31 (MeOD), 2.05 (acetone-d₆); ¹³C δ = 77.0 (CDCl₃), 39.43 (DMSO-d₆), 49.05 (MeOD), 29.84 (acetone-d₆). Coupling constants (*J*) are given in Hz. Triethylphosphine, fumaronitrile, and boron trifluoride diethyl etherate were obtained from Sigma-Aldrich. Indoles **1a-g** were obtained from Matrix Scientific.

For photophysical measurements, UV-vis spectra were recorded with a diode-array spectrometer fiber-optically coupled to tungsten and incandescent deuterium light sources (Stellarnet). Fluorescence spectra were collected with a PERKIN-ELMER LS-5B Luminescence Spectrometer. Sample solutions were placed in a 10-mm pathlength cuvette for both absorption and emission experiments. In fluorescence quantum yield measurements, tyrosine¹ and quaterthiophene² served as standards for excitation at 270 and 370 nm, respectively. Typically, fluorescence intensities under six different concentrations were collected. The R square values for linear fits to concentration-dependent fluorescence intensities were > 0.99 in all cases.

1.2 Preparation of Benzo[1,2-b]indolizines 3a-h



General Procedure. To a stirring solution of the indole-2-aldehyde (0.69 mmol) in THF (1.4 mL) was added fumaronitrile (67 mg, 0.86 mmol), followed by triethylphosphine (122 μ L, 0.83 mL) dropwise. The reaction mixture was heated to 65 °C and stirred for 8 h. The crude mixture was cooled to room temperature, and a catalytic amount of KOH (15 mg, 0.28 mmol) was added as a single portion. The reaction mixture was stirred for 30 minutes, then quenched with saturated aqueous ammonium chloride and extracted with EtOAc (3 × 15 mL). The combined organic extracts were washed with brine, dried over sodium sulfate, and concentrated *in vacuo*. Purification by flash chromatography (~20% acetone in petroleum ether) afforded the substituted benzoindolizines **3a-g**.

6-Aminobenzo[1,2-*b***]indolizine-8-carbonitrile (3a).** 90% yield; mp 221-222 °C; ¹H-NMR (400 MHz; acetone-d₆): δ 8.51 (d, J = 8.0 Hz, 1H), 7.83 (d, J = 8.0 Hz, 1H), 7.55 (s, 1H), 7.39 (t, J = 7.9 Hz, 1H), 7.29 (t, J = 8.0 Hz, 1H), 6.98 (s, 1H), 6.18 (s, 2H), 5.99 (s, 1H); ¹³C-NMR (101 MHz, acetone-d₆): δ 147.8, 137.4, 131.6, 131.3, 124.1, 121.3, 119.7, 116.5, 115.9, 115.9, 107.3, 97.2, 88.4; HRMS (FAB) calcd for C₁₃H₉N₃ [M]+, 207.0797; found, 207.0791.



6-Amino-2-methylbenzo[1,2-*b*]indolizine-8-carbonitrile (3b). 87% yield; mp 238-239 °C; ¹H-NMR (400 MHz; acetone-d₆): δ 8.37 (d, *J* = 8.5 Hz, 1H), 7.60 (s, 1H), 7.51 (s, 1H), 7.13 (d, *J* = 8.5 Hz, 1H), 6.88 (s, 1H), 6.13 (s, 2H), 5.96 (s, 1H), 2.49 (s, 3H); ¹³C-NMR (101 MHz, 101 MHz).

acetone-d₆): δ 147.6, 137.5, 133.5, 132.0, 129.7, 123.2, 120.6, 119.8, 116.0, 115.7, 107.0, 96.7, 88.1, 21.6; HRMS (FAB) calcd for C₁₄H₁₁N₃ [M]+, 221.0953; found, 221.0958.



6-Amino-2-methoxybenzo[**1,2-***b*]**indolizine-8-carbonitrile (3c).** 86% yield; mp 197-198 °C; ¹H-NMR (400 MHz; acetone-d₆): δ 8.38 (d, J = 9.4 Hz, 1H), 7.50 (s, 1H), 7.25 (d, J = 2.5 Hz, 1H), 6.92–6.89 (m, 2H), 6.12 (s, 2H), 5.98 (s, 1H), 3.88 (s, 3H); ¹³C-NMR (101 MHz, acetone-

d₆): δ 157.3, 147.3, 138.0, 132.9, 126.5, 119.8, 117.4, 115.2, 112.4, 106.8, 100.9, 96.8, 88.5, 55.7; HRMS (FAB) calcd for C₁₄H₁₁N₃O [M]+, 237.0902; found, 237.0900.



6-Amino-2-fluorobenzo[1,2-*b*]indolizine-8-carbonitrile (3d). 62% yield; mp 207-208 °C; ¹H-NMR (400 MHz; acetone-d₆): δ 8.54 (dd, J = 9.5, 4.5 Hz, 1H), 7.57 (d, J = 1.5 Hz, 1H), 7.50 (dd, J = 9.5, 2.7 Hz, 1H), 7.07 (td, J = 9.2, 2.7 Hz, 1H), 6.98 (s, 1H), 6.22 (s, 2H), 6.06 (d, J = 1.5 Hz, 1H); ¹³C-

NMR (101 MHz, acetone-d₆): δ 159.3 (d, J = 238.9 Hz), 146.8, 138.0, 131.6 (d, J = 11.1 Hz), 127.2, 118.6, 117.2 (d, J = 9.9 Hz), 114.5, 108.7 (d, J = 26.6 Hz), 107.1, 104.0 (d, J = 23.5 Hz), 96.2 (d, J = 5.1 Hz), 88.3; HRMS (FAB) calcd for C₁₃H₈FN₃ [M]+, 225.0702; found, 225.0702.



6-Amino-3-bromobenzo[**1**,**2**-*b*]**indolizine-8-carbonitrile (3e).** 66% yield; mp 199-200 °C; ¹H-NMR (400 MHz, acetone-d₆): δ 8.71 (m, 1H), 7.80 (d, J = 8.6 Hz, 1H), 7.60 (d, J = 1.2 Hz, 1H), 7.52 (dd, J = 8.6, 1.6 Hz, 1H), 7.01 (s, 1H), 6.26 (s, 2H), 6.06 (d, J = 1.6 Hz, 1H); ¹³C-NMR (101 MHz, 101 MHz), 6.06 (d, J = 1.6 Hz, 1H); ¹³C-NMR (101 MHz), 6.06 (d, J = 1.6 Hz, 1H); ¹³C-NMR (101 MHz), 6.06 (d, J = 1.6 Hz, 1H); ¹³C-NMR (101 MHz), 6.06 (d, J = 1.6 Hz, 1H); ¹³C-NMR (101 MHz), 6.06 (d, J = 1.6 Hz, 1H); ¹³C-NMR (101 MHz), 6.06 (d, J = 1.6 Hz, 1H); ¹³C-NMR (101 MHz), 6.06 (d, J = 1.6 Hz, 1H); ¹³C-NMR (101 MHz), 6.06 (d, J = 1.6 Hz, 1H); ¹³C-NMR (101 MHz), 6.06 (d, J = 1.6 Hz, 1H); ¹³C-NMR (101 MHz), 6.06 (d, J = 1.6 Hz, 1H); ¹³C-NMR (101 MHz), 6.06 (d, J = 1.6 Hz, 1H); ¹³C-NMR (101 MHz), 6.06 (d, J = 1.6 Hz, 1H); ¹³C-NMR (101 MHz), 6.06 (d, J = 1.6 Hz, 1H); ¹³C-NMR (101 MHz), 6.06 (d, J = 1.6 Hz), 6.06 (d, J = 1.6 Hz

acetone-d₆): δ 147.6, 138.0, 131.6, 130.2, 127.2, 122.6, 119.4, 119.2, 116.3, 113.7, 107.9, 97.4, 89.5; HRMS (FAB) calcd for C₁₃H₈⁷⁹BrN₃ [M]+, 284.9902; found, 284.9895; calcd for C₁₃H₈⁸¹BrN₃ [M]+, 286.9881; found, 286.9880.



6-Amino-3-chloro-4-methylbenzo[1,2-*b*]**indolizine-8-carbonitrile** (3**f**). 41% yield; mp 190-191 °C; ¹H-NMR (400 MHz; acetone-d₆): δ 7.61 (d, J = 8.4 Hz, 1H), 7.41 (d, J = 8.4 Hz, 1H), 7.36 (s, 1H), 6.84 (s, 1H), 6.18 2H), 5.79 (s, 1H), 2.81 (s, 3H); ¹³C-NMR (101 MHz, acetone-d₆): δ 149.6, 139.6, 131.9, 131.7, 129.3, 126.3, 124.7, 119.6, 119.5, 114.8, 108.5, 98.3, 86.6, 22.1; HRMS (FAB) calcd for C₁₄H₇ClF₃N₃ [M]+, 255.0563; found, 255.059.

2 NMR Spectra



1H-NMR spectrum for compound 3a (Acetone-d6, 400 MHz)











13C-NMR spectrum for compound 3b (Acetone-ds, 100 MHz)







13C-NMR spectrum for compound 3c (Acetone-ds, 100 MHz)





















13C-NMR spectrum for compound 3f (Acetone-ds, 100 MHz)



3 Photophysical Properties

3.1 Optical Properties of Neutral Benzo[1,2-b]indolizines

Figure S1. Normalized UV-vis spectra of 3a-d and 3f in methanol.

Figure S2. Normalized fluorescence spectra excited at 370 nm of 3a-d and 3f in methanol.

3.2 Acid-Responsive Optical Properties of Benzo[1,2-b]indolizines

Figure S3. Fluorescence spectra excited at 370 nm of (a) 3a, (b) 3d and (c) 3f with TFA (vol %) titration in methanol.

Figure S4. (a) UV-vis and (b) fluorescence spectra excited at 370 nm of **3b** before (black) and after (red) addition of excessive amount of triethylamine (Et₃N) in methanol.

Figure S5. Normalized fluorescence spectra of protonated (a) **3b** and (b) **3c** dissolved in CH₃CN, CHCl₃, toluene and CH₃OH excited at 360 nm.

3.3 Theoretical Calculations

All calculations were performed at the CAM-B3LYP/6-31G*/PCM (methanol) level using the Gaussian 09 package.³ No imaginary frequencies were found at the optimized geometries.

3.3.1 Ground state optimized geometry, frontier molecular orbitals, and calculated UV-Vis spectrum of 3b

Figure S6. Optimized structures of 3b.

Figure S7. Molecular orbitals of 3b.

Figure S8. Calculated UV-vis spectrum of 3b by TD-DFT.

3.3.2 Ground state optimized geometries and corresponding energies of three protonated

3b tautomers

The NMR spectrum of the protonated **3b** from Figure 4 in the main text indicates two potential tautomeric structures: protonation either on C-7 (T1) or C-9 (T2). Here we optimize the ground state geometries of T1 and T2, as well as the amine protonation structure (N). Their corresponding energies are tabulated in Table S1. It is predicted that T1 is the most energetically favored tautomer, in good agreement with the NMR result.

Figure S9. S₀ optimized structure of N viewed from top (above) and side (bottom).

Figure S10. S₀ optimized structure of T1 viewed from top (above) and side (bottom).

Figure S11. S₀ optimized structure of T2 viewed from top (above) and side (bottom).

Table S1.	Calculated	ground state	energies	of the tautomer	rs of 3b	(N. T1	and T2) in CH ₃ OH
		C				X 2	,	/ -)-

tautomer	S0 $(eV)^a$			
Ν	0.68			
T1	0			
T2	0.19			

^{*a*} DFT at CAM-B3LYP/6-31G*/PCM level. The energy of T1 has been set to 0.

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