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Meso-pyridyl BODIPYs with tunable chemical, optical and electrochemical properties

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Supporting Information

Additional Experimental Details and Results

Fluorescence quantum yields were determined by the comparative method of Williams *et al*.[S1] The integrated fluorescence intensities of a known dye and the tested compound were compared and fluorescence quantum yields were calculated using the following equation: $\Phi_x = (\Phi_{st}) (Grad_x / Grad_{st}) (\eta^2_x / \eta^2_{st})$

st and x denotes the standard and test respectively, while Φ is the fluorescence quantum yield. *Grad* is the gradient obtained from the plot of integrated fluorescence intensity *vs.* absorbance of the dye at the excitation wavelength. η represents the refractive index of the used solvents. The reference dye for the measurements in dichloromethane was BODIPY **1**, with a reported fluorescence quantum yield of 0.30 (in dichloromethane).[S2]

To determine the pH dependent fluorescence of BODIPY **1**-**5**, a set of buffer solutions was prepared. Either acetic acid/acetate or trifluoroacetic acid/trifluoroacetate buffers, in a solvent of mixture of 25% water and 75% methanol, were used. This solvent mixture is necessary to ensure a good solubility of the BODIPYs. The pH values measured ranged from pH 1.33 to pH 6.53. The investigated pH range for the buffers reached the lower limit determined by the lowest pH possible with the used buffer systems (0.1 M; including 95% trifluoroacetic acid : 5% potassium trifluoroacetate solution). If a compound showed no further increase (or decrease) of the fluorescence emission, no further measurements were carried out.

All samples were excited at 440 nm, ensuring a constant absorption throughout a set of fluorescence measurements, which was monitored by additional absorption measurements. Care was taken to ensure that the maximum absorbance did not exceed 0.1 in the region of the emission, to eliminate fluorescence quenching due to self-absorption of the dye.

All fluorescence spectra obtained were integrated, and the fluorescence spectrum with the maximum value of integrated fluorescence intensity was set to be 1. Dependent on this, all spectra of one set of experiments were normalized relative to the maximum value. A plot of all sets of data for one compound, normalized integrated fluorescence intensity *vs*. pH, shows a titration curve and allows an estimation of the basicity of the investigated BODIPYs. It is worth to mention that a certain offset of the integrated fluorescence intensity is observable, which is due to the background signal of the fluorescence spectrometer. This value can be seen as a constant throughout the whole set of experiments and does not influence the interpretation of the obtained trends.

Reversibility of the protonation was probed by determining the emission intensity of a given sample of **1**-**5** in a 0.1 M sodium acetate solution (pH 8.25) and in a 0.1 M trifluoroacetic acid solution of pH 1.85 (solvent methanol/water 3:1 v/v). The trifluoacetic acid solution was then neutralized with conc. NaOH (aq) and the fluorescence intensity was determined again – a full recovery of the fluorescence intensity has been observed.

Crystallographic details

Table S1. *Crystal data and structure refinement for* ***2.***

Empirical formula	$C_{18}\,H_{17}\,B\,Cl\,F_2\,N_3$	
Formula weight	359.61	
Temperature	100(1) K	
Wavelength	1.54184 Å	
Crystal system	Monoclinic	
Space group	$P2_1/n$	
Unit cell dimensions	a = 7.36780(10) Å	α= 90°.
	b = 22.1323(3) Å	β= 109.642(2)°.
	c = 10.9276(2) Å	γ = 90°.
Volume	1678.24(4) $Å^3$	
Z	4	
Density (calculated)	1.423 Mg/m^3	
Absorption coefficient	2.247 mm^{-1}	
F(000)	744	
Crystal size	0.04 x 0.17 x 0.35 mm^3	
Theta range for data collection	3.99 to 67.10°.	
Index ranges	-8<=h<=8, -26<=k<=26, -13<=l<=13	
Reflections collected	34862	
Independent reflections	2981 [R(int) = 0.0383]	
Completeness to theta = 67.10°	99.9 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2981 / 0 / 230	
Goodness-of-fit on F^2	1.085	
Final R indices [I>2sigma(I)]	R1 = 0.0352, wR2 = 0.0918	
R indices (all data)	R1 = 0.0372, wR2 = 0.0933	
Largest diff. peak and hole	0.614 and -0.340 $e.Å^{-3}$	
CCDC	935208	

This crystal was used for measurement on an Agilent Gemini Ultra diffractometer with Cu Kα radiation (λ = 1.54184 Å) at 100(1) K.. The crystal structure was solved by direct methods (*SHELXS*-97) and expanded using difference Fourier techniques. The structure was refined with *SHELXL*-97 using full-matrix least-squares calculations.

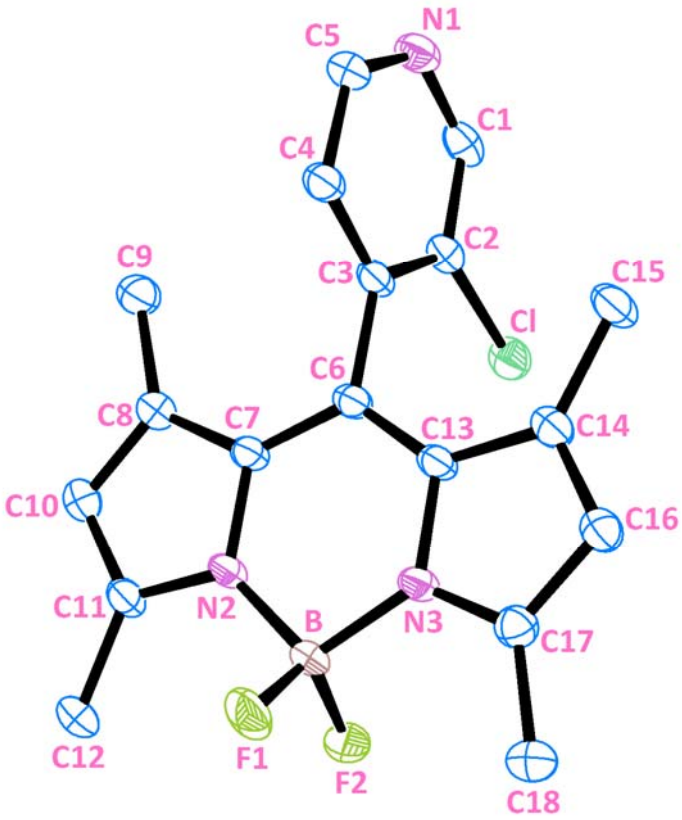


Fig. S1 *Crystal structure of* ***2****.*

Table S2. *Crystal data and structure refinement for* ***3***

Empirical formula	$C_{18}H_{16}BCl_2F_2N_3$	
Formula weight	394.05	
Temperature	100(1) K	
Wavelength	1.54184 Å	
Crystal system	Monoclinic	
Space group	C2/c	
Unit cell dimensions	a = 20.3327(3) Å	α= 90°.
	b = 7.29560(10) Å	β= 114.731(2)°.
	c = 26.1828(5) Å	γ = 90°.
Volume	3527.71(10) $Å^3$	
Z	8	
Density (calculated)	1.484 Mg/m^3	
Absorption coefficient	3.552 mm^{-1}	
F(000)	1616	
Crystal size	0.24 x 0.21 x 0.09 mm^3	
Theta range for data collection	3.72 to 67.09°.	
Index ranges	-24<=h<=24, -8<=k<=8, -31<=l<=29	
Reflections collected	30627	
Independent reflections	3146 [R(int) = 0.0267]	
Completeness to theta = 67.09°	99.9 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3146 / 0 / 239	
Goodness-of-fit on F^2	1.049	
Final R indices [I>2sigma(I)]	R1 = 0.0250, wR2 = 0.0660	
R indices (all data)	R1 = 0.0261, wR2 = 0.0670	
Largest diff. peak and hole	0.250 and -0.224 $e.Å^{-3}$	
CCDC	935207	

This crystal was used for measurement on an Agilent Gemini Ultra diffractometer with Cu Kα radiation (λ = 1.54184 Å) at 100(1) K. The crystal structure was solved by direct methods (*SHELXS*-97) and expanded using difference Fourier techniques. The structure was refined with *SHELXL*-97 using full-matrix least-squares calculations.

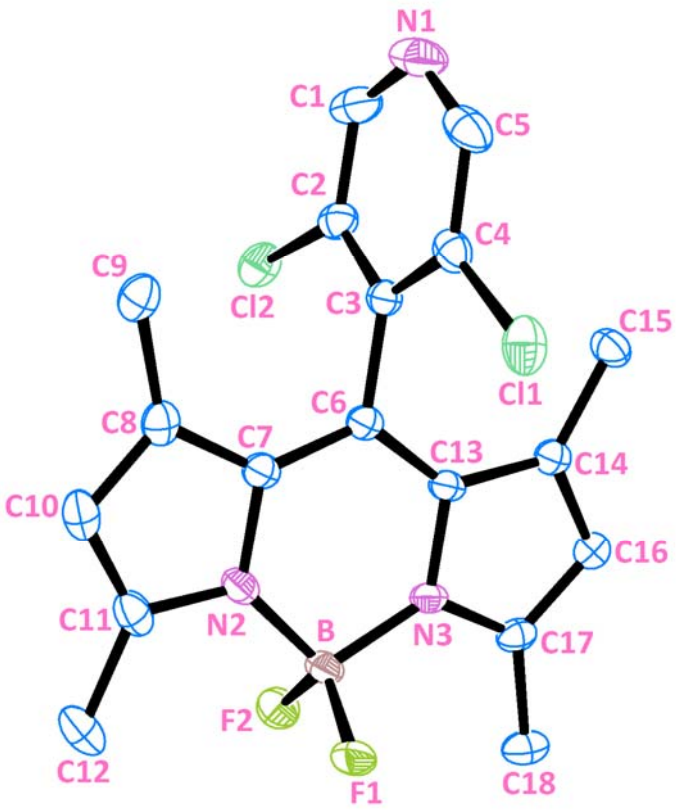


Fig. S2 *Crystal structure of* ***3****.*

Synthetic Procedures

1 (1,3,5,7-tetramethyl-8-(4-pyridyl)-4,4'-difluoroboradiazaindacene) was synthesized following a previously published protocol, which represents procedure A in 30% yield.[S2]

Procedure A

The substituted pyridine-4-carboxaldehyde and two equivalents of 2,4-dimethylpyrrole were dissolved under N_2 atmosphere in dichloromethane. To start the reaction, several drops of trifluoroacetic acid were added and the mixture was stirred for 3 days. TLC monitoring of the aldehyde consumption is insufficient for following reaction completion, presumably due to the presence of protonated pyridine-carboxaldehyde. Chloranil was added and the reaction mixture was stirred for additional 2 h, followed by subsequent addition of diisopropylethylamine (DiPEA). After stirring another 30 min, borontrifluoride etherate was added and stirred again for 3 h. The dark red precipitate that formed was filtered off using a pad of basic alumina (activity grade I), the filtrate was reduced under vacuum and separated by column chromatography (SiO_2) eluting the product as strongly fluorescent fraction with dichloromethane and rising amounts of ethyl acetate, unless otherwise noted.

2 (1,3,5,7-tetramethyl-8-(2-chloro-4-pyridyl)-4,4'-difluoroboradiazaindacene)

2,4-Dimethylpyrrole: 0.66 g, 7.0 mmol

3-chloropyridine-4-carboxaldehyde: 0.50 g, 3.53 mmol

200 mL dichloromethane

chloranil: 0.852 g

DiPEA: 3.65 mL

borontrifluoride etherate: 3.88 mL

yield: 26%; orange, micro-crystalline powder (325 mg, 0.905 mmol)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.77 (s, 1H), 8.66 (d, 1H, J = 4.8 Hz), 7.31 (d, 1H, J = 5.3 Hz), 6.02 (s, 2H), 2.57 (s, 6H), 1.45 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 13.9, 14.7, 121.9, 124.5, 129.9, 131.2, 134.1, 142.1, 142.3, 148.5, 150.4, 157.0.

^{19}F NMR (376 MHz, $CDCl_3$) δ -146.64 (m, 2F, J (F^a-F^b) = 129.6 Hz, J (^{11}B-F^a) = 34.6 Hz, J (^{11}B-F^b) = 30.2 Hz,).

UV-Vis (CH_2Cl_2) λ_{max} (ε [x10^3 M^{-1} cm^{-1}]) 312 (4.6), 371 (4.9), 479s (20.1), 510 (83.2) nm.

UV-Vis (methanol) λ_{max} (ε [x10^3 M^{-1} cm^{-1}]) 311 (5.4), 371 (5.7), 477s (23.7), 507 (92.7) nm.

HRMS-ESI: *m/z*: calcd for $C_{18}H_{18}BClF_2N_3$: 359.1281 [M], found: 359.1291.

3 (1,3,5,7-tetramethyl-8-(2,5-dichloro-4-pyridyl)-4,4'-difluoroboradiazaindacene)

2,4-Dimethylpyrrole: 1.081 g, 11.36 mmol

3,5-dichloropyridine-4-carboxaldehyde: 1.00 g, 5.68 mmol

300 mL dichloromethane

chloranil: 1.40 g

DiPEA: 5.87 mL

borontrifluoride etherate: 6.23 mL

yield: 3%; orange, micro-crystalline powder (67 mg, 0.170 mmol)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.67 (s, 2H), 6.03 (s, 2H), 2.58 (s, 6H), 1.50 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 13.4, 14.8, 121.9, 129.2, 131.3, 132.1, 141.1, 141.3, 148.1, 157.5.

^{19}F NMR (376 MHz, $CDCl_3$) δ -146.69 (q, 2F, *J* (B-F) = 33.1 Hz).

UV-Vis (CH_2Cl_2) λ_{max} (ε [x10^3 M^{-1} cm^{-1}]) 312 (4.8), 374 (4.3), 484s (18.8), 515 (73.4) nm.

UV-Vis (methanol) λ_{max} (ε [x10^3 M^{-1} cm^{-1}]) 314 (4.7), 373 (4.8), 482s (20.9), 512 (83.3) nm.

HRMS-ESI: *m/z*: calcd for $C_{18}H_{16}BCl_2F_2N_3$: 394.0859 [M+H], found: 394.0859.

4 (1,3,5,7-tetramethyl-8-(2-fluoro-4-pyridyl)-4,4'-difluoroboradiazaindacene)

2,4-Dimethylpyrrole: 0.761 g, 8.00 mmol

3-fluoropyridine-4-carboxaldehyde: 0.50 g, 4.00 mmol

200 mL dichloromethane

chloranil: 0.980 g

DiPEA: 4.12 mL

borontrifluoride etherate: 4.39 mL

A second chromatography column (SiO_2), eluting with toluene/ethylacetate (5:1), was required to purify the product.

yield: 18%; orange, micro-crystalline powder (246 mg, 0.717 mmol)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.65 (s, 1H), 8.60 (d, 1H, *J* = 4.4 Hz), 7.32 (d, 1H, *J* = 5.3 Hz), 6.03 (s, 2H), 2.56 (s, 6H), 1.48 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 14.0, 14.7, 122.0, 125.9, 130.4, 130.8/131.0 (d, 1C, ^2J = 17.5 Hz), 130.8, 139.2/139.4 (d, 1C, ^2J = 23.7 Hz), 142.2, 146.5/146.6 (d, 1C, ^3J = 5.3 Hz), 155.0/157.6 ((d, 1C, ^1J = 156.5 Hz), 157.0.

^{19}F NMR (376 MHz, $CDCl_3$) δ -128.71 (s, 1F), -146.62 (m, 2F, J (F^a-F^b) = 106.5 Hz, J (^{11}B-F^a) = 33.1, Hz, J (^{11}B-F^b) = 30.2 Hz,).

UV-Vis (CH_2Cl_2) λ_{max} (ε [x10^3 M^{-1} cm^{-1}]) 312 (4.6), 370 (4.7), 480s (18.9), 510 (75.9) nm.

UV-Vis (methanol) λ_{max} (ε [x10^3 M^{-1} cm^{-1}]) 311 (5.7), 370 (5.8), 478s (24.2), 507 (92.2) nm.

HRMS-ESI: *m/z*: calcd for $C_{18}H_{17}BF_3N_3$: 344.1544 [M+H], found: 344.1536.

5(1,3,5,7-tetramethyl-8-(2-methyl-4-pyridyl)-4,4'-difluoroboradiazaindacene)

2,4-Dimethylpyrrole: 0.786 g, 8.26 mmol

3-methylpyridine-4-carboxaldehyde: 0.50 g, 4.13 mmol

200 mL dichloromethane

chloranil: 1.015 g

DiPEA: 4.27 mL

borontrifluoride etherate: 4.53 mL

A second chromatography column (SiO_2), eluting with diethyl ether, was required to purify the product.

yield: 26%; orange, micro-crystalline powder (363 mg, 1.070 mmol)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.60 (m, 2H), 7.18 (d, 1H, J = 4.9 Hz), 6.01 (s, 2H), 2.57 (s, 6H), 2.23 (s, 3H), 1.39 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 14.0, 14.7, 16.1, 121.6, 122.8, 129.8, 131.2, 137.3, 142.2, 142.9, 148.3, 151.7, 156.5.

^{19}F NMR (376 MHz, $CDCl_3$) δ -146.64 (m, 2F)

UV-Vis (CH_2Cl_2) λ_{max} (ε [x10^3 M^{-1} cm^{-1}]) 310 (4.5), 366 (4.4), 475s (17.9), 505 (75.4) nm.

UV-Vis (methanol) λ_{max} (ε [x10^3 M^{-1} cm^{-1}]) 310 (4.4), 367 (4.9), 473s (19.7), 502 (79.1) nm.

HRMS-ESI: *m/z*: calcd for $C_{19}H_{20}BF_2N_3$: 340.1795 [M+H], found: 340.1793.

Procedure B

As described in the main text of the manuscript.

1 (1,3,5,7-tetramethyl-8-(4-pyridyl)-4,4'-difluoroboradiazaindacene)

2,4-Dimethylpyrrole: 1.081 g, 11.36 mmol

pyridine-4-carboxaldehyde: 0.608 g, 5.68 mmol

280 mL dichloromethane + 20 mL ethanol

chloranil: 1.396 g

DiPEA: 5.87 mL

borontrifluoride etherate: 6.23 mL

yield: 46 %; orange, micro-crystalline powder (847 mg, 2.605 mmol)

^{19}F NMR (376 MHz, $CDCl_3$) δ -146.71 (q, 2F, *J* (B-F) = 31.7 Hz)

UV-Vis (methanol) λ_{max} (ε [x10^3 M^{-1} cm^{-1}]) 310 (4.5), 367 (4.8), 472s (18.7), 502 (76.7) nm.

2 (1,3,5,7-tetramethyl-8-(2-chloro-4-pyridyl)-4,4'-difluoroboradiazaindacene)

2,4-Dimethylpyrrole: 1.081 g, 11.36 mmol

3-chloropyridine-4-carboxaldehyde: 0.830 g, 5.68 mmol

280 mL dichloromethane + 20 mL ethanol

chloranil: 1.396 g

DiPEA: 5.87 mL

borontrifluoride etherate: 6.23 mL

yield: 34 %; orange, micro-crystalline powder (713 mg, 1.985 mmol)

3 (1,3,5,7-tetramethyl-8-(2,5-dichloro-4-pyridyl)-4,4'-difluoroboradiazaindacene)

2,4-Dimethylpyrrole: 1.081 g, 11.36 mmol

3,5-dichloropyridine-4-carboxaldehyde: 1.00 g, 5.68 mmol

280 mL dichloromethane + 20 mL ethanol

chloranil: 1.40 g

DiPEA: 5.87 mL

borontrifluoride etherate: 6.23 mL

yield: 20 %; orange, micro-crystalline powder (465 mg, 1.157 mmol)

4 (1,3,5,7-tetramethyl-8-(2-fluoro-4-pyridyl)-4,4'-difluoroboradiazaindacene)

2,4-Dimethylpyrrole: 0.761 g, 8.00 mmol

3-fluoropyridine-4-carboxaldehyde: 0.500 g, 4.00 mmol

140 mL dichloromethane + 10 mL ethanol

chloranil: 0.980 g

DiPEA: 4.12 mL

borontrifluoride etherate: 4.39 mL

yield: 50 %; orange, micro-crystalline powder (689 mg, 2.008 mmol)

5 (1,3,5,7-tetramethyl-8-(2-methyl-4-pyridyl)-4,4'-difluoroboradiazaindacene)

2,4-Dimethylpyrrole: 0.786 g, 8.26 mmol

3-methylpyridine-4-carboxaldehyde: 0.500 g, 4.13 mmol

140 mL dichloromethane + 10 mL ethanol

chloranil: 1.015 g

DiPEA: 4.27 mL

borontrifluoride etherate: 4.53 mL

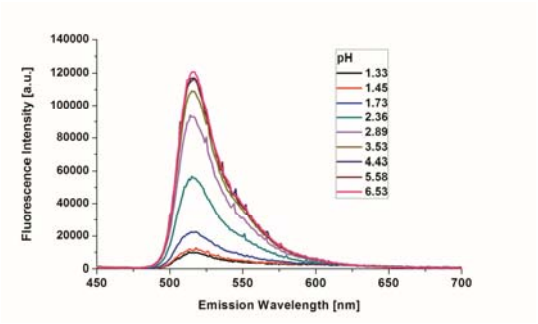
yield: 30 %; orange, micro-crystalline powder (422 mg, 1,244 mmol)

References

[S1] Williams, A. T. R.; Winfield, S. A.; Miller, J. N. *Analyst* **1983**, *108*, 1067-1071.

[S2] Bartelmess, J. and Weare, W. W. *Dyes Pigm.* **2013**, *97*, 1-8.

1



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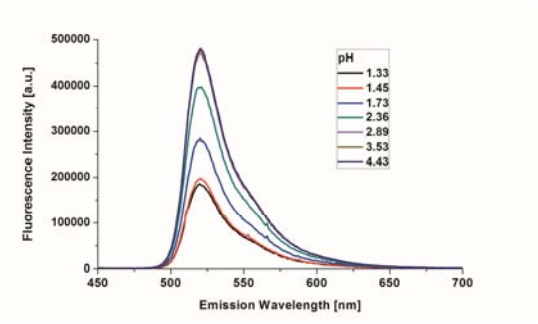

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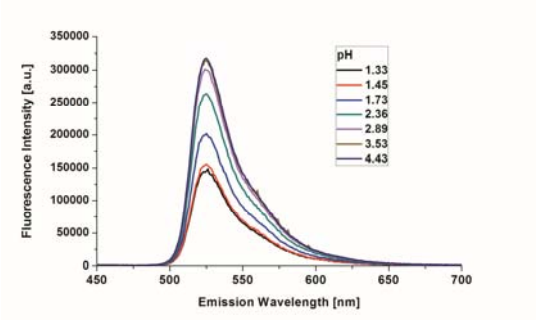

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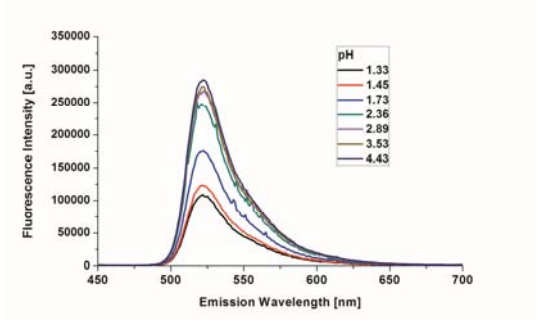

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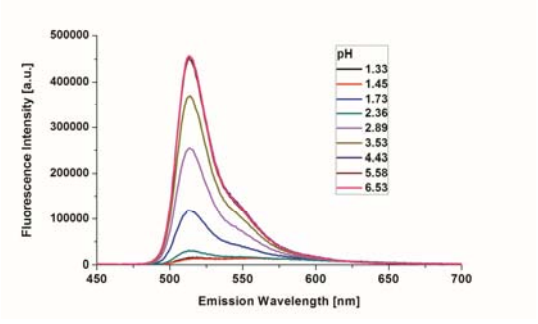

Fig. S3 *Plot of the fluorescence spectra of compounds **1**-**5** in different buffer solutions (solvent: 25% H_2O / 75% methanol; buffer: trifluoroacetic acid / trifluoroacetate or acetic acid /acetate) of distinct pH. Excitation wavelength 440 nm.*

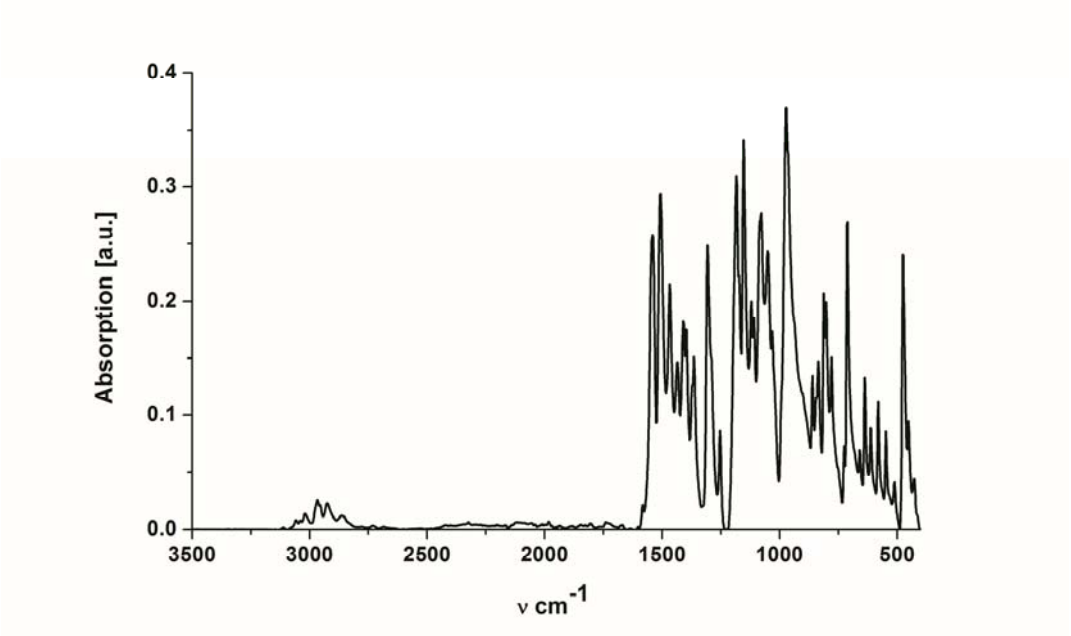

Fig. S4 *Solid state ATR-FT-IR spectrum of* ***2****.*

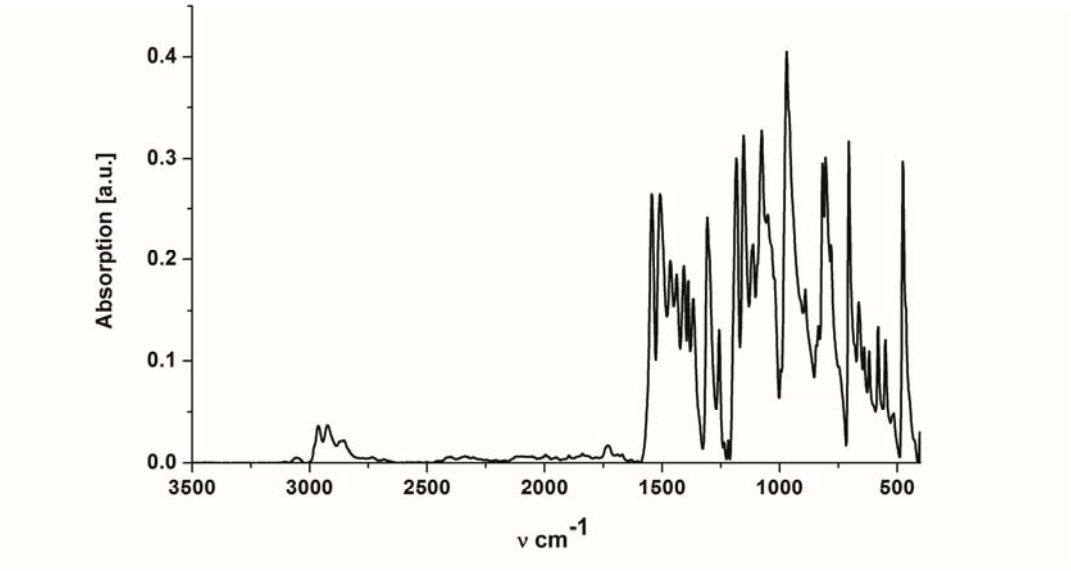

Fig. S5 *Solid state ATR-FT-IR spectrum of* ***3****.*

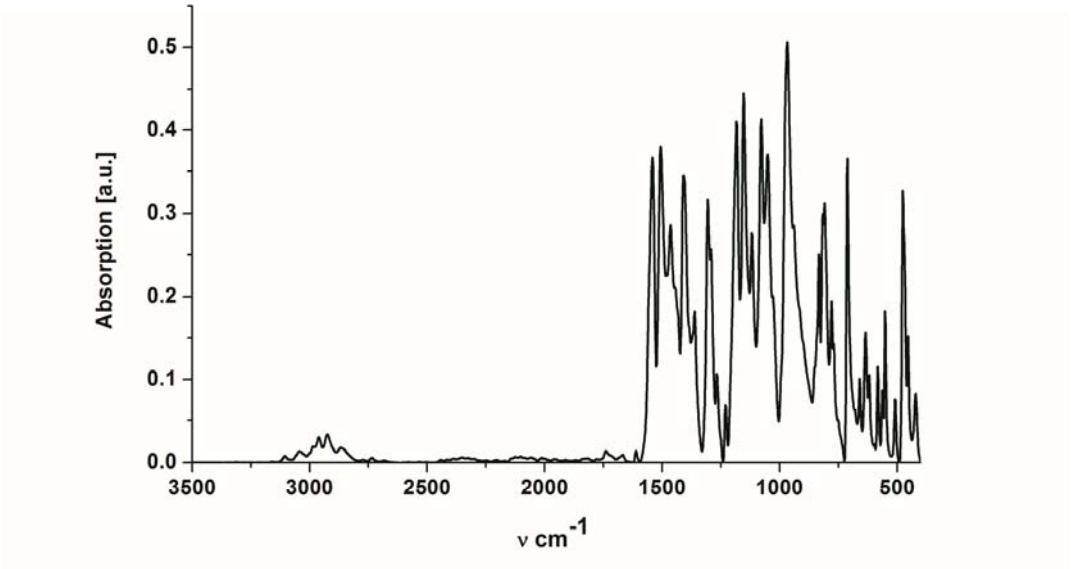

Fig. S6 *Solid state ATR-FT-IR spectrum of* ***4****.*

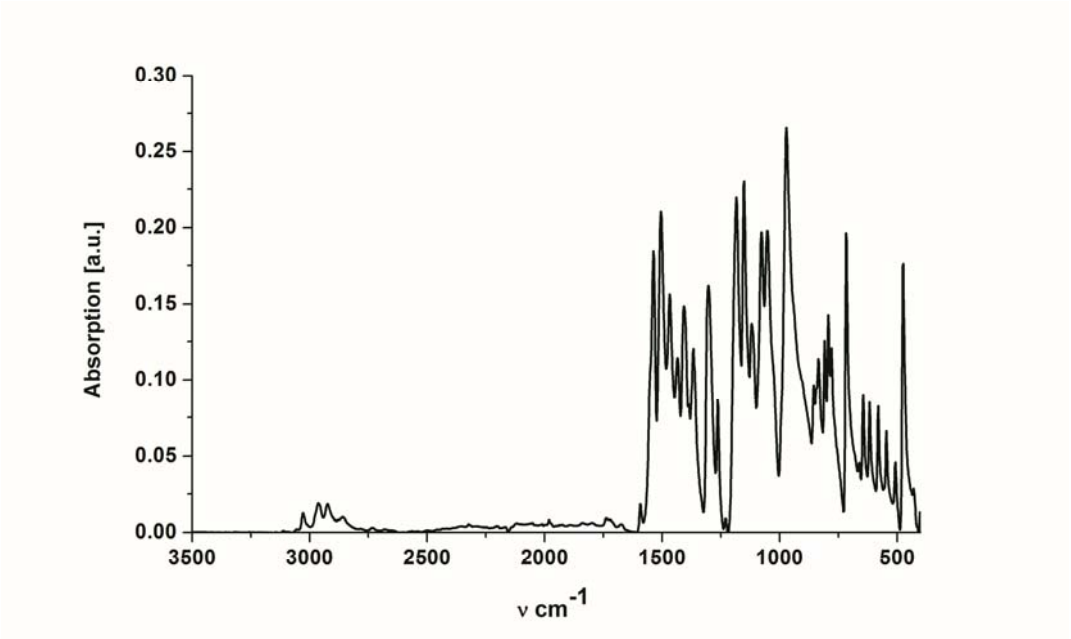

Fig. S7 *Solid state ATR-FT-IR spectrum of* ***5****.*

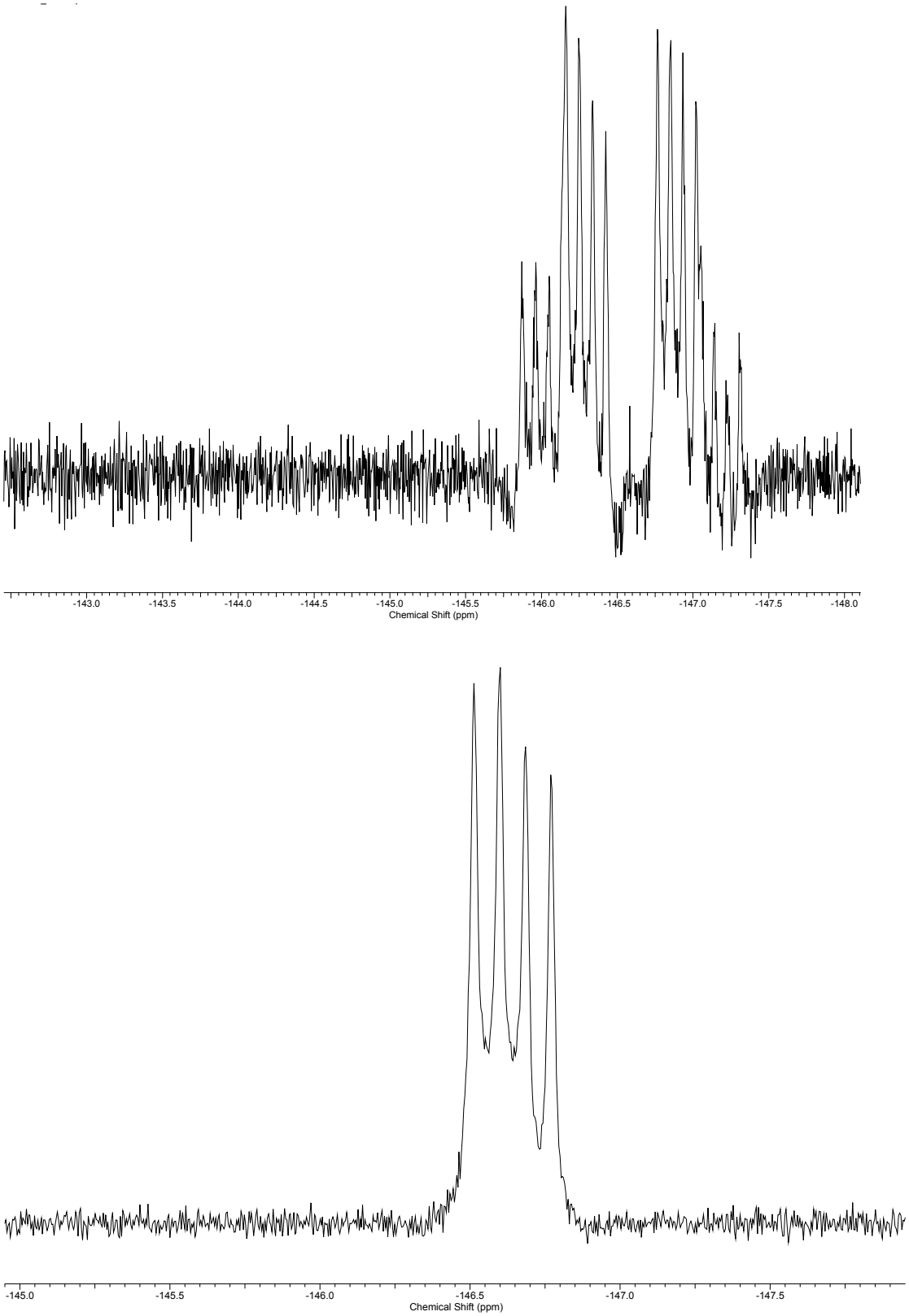

Figure S8. *^{19}F NMR spectra of compounds **2** (top) and **3** (bottom).*

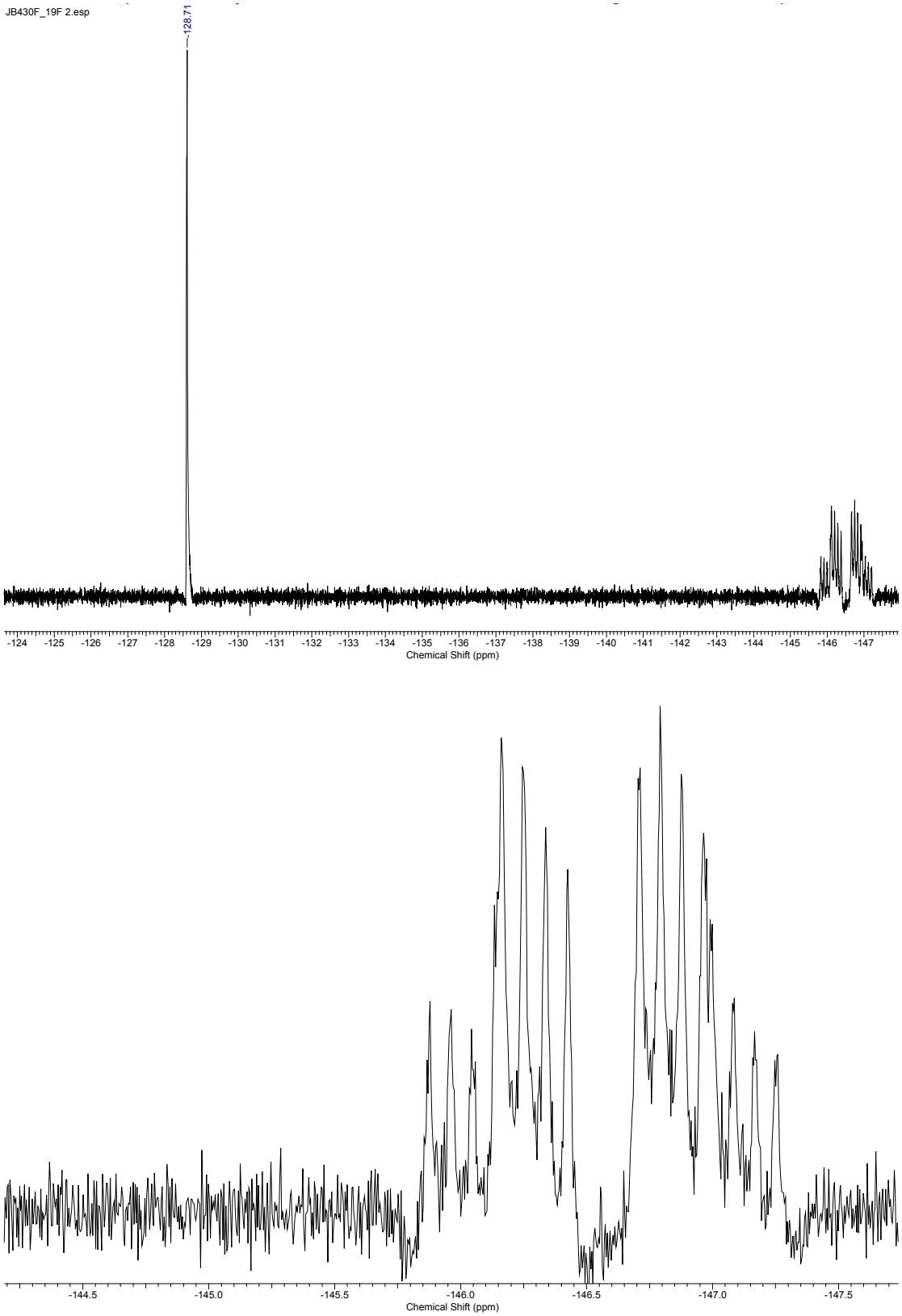

Figure S9. *^{19}F NMR spectra of compound* ***4****.*