Electronic Supplementary Material (ESI) for Analytical Methods.

A novel near-infrared colorimetric and fluorescent probe based on piperidine-substituted aza-BODIPY photosensitizer for detection of extreme acidity

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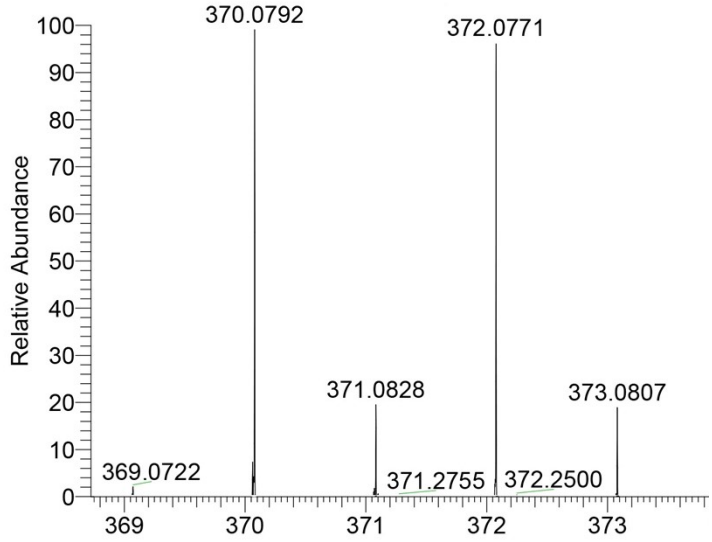


Fig. S1 The HR-MS spectrum of **1**.

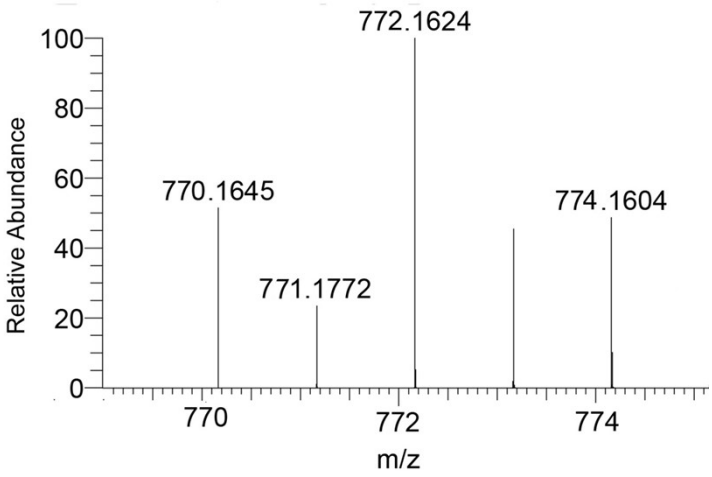


Fig. S2 The HR-MS spectrum of **3**.

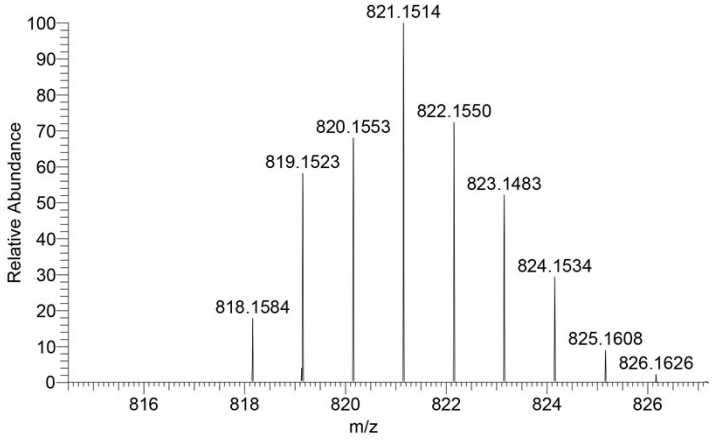


Fig. S3 The HR-MS spectrum of Probe 1.

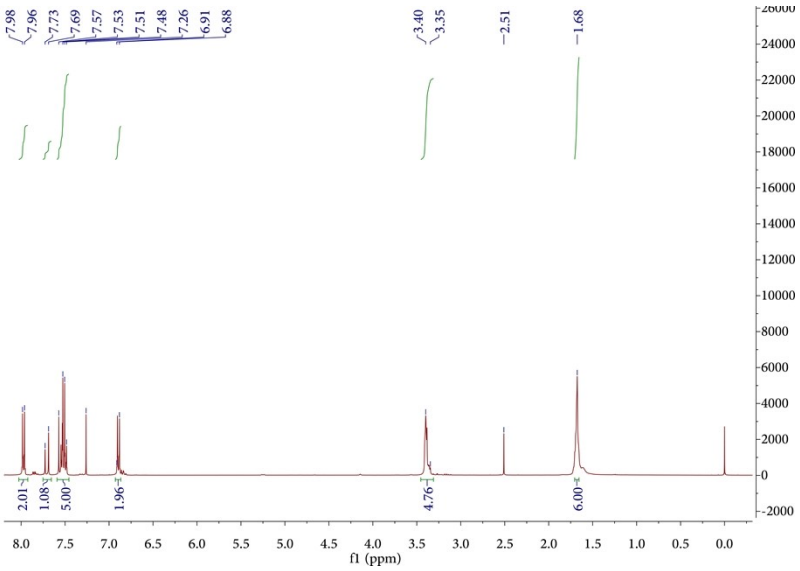


Fig. S4 The ^{1}H NMR spectrum of **1** in $CDCl_3$.

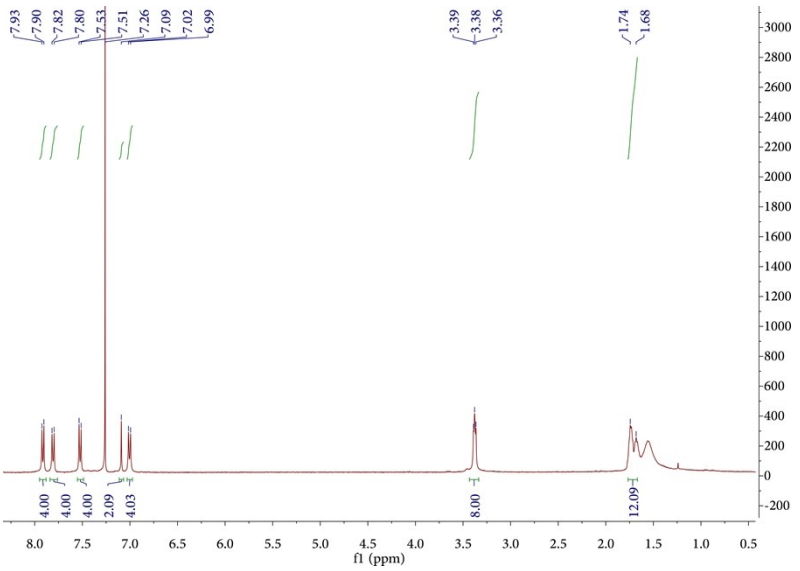


Fig. S5 The ^{1}H NMR spectrum of **3** in $CDCl_3$.

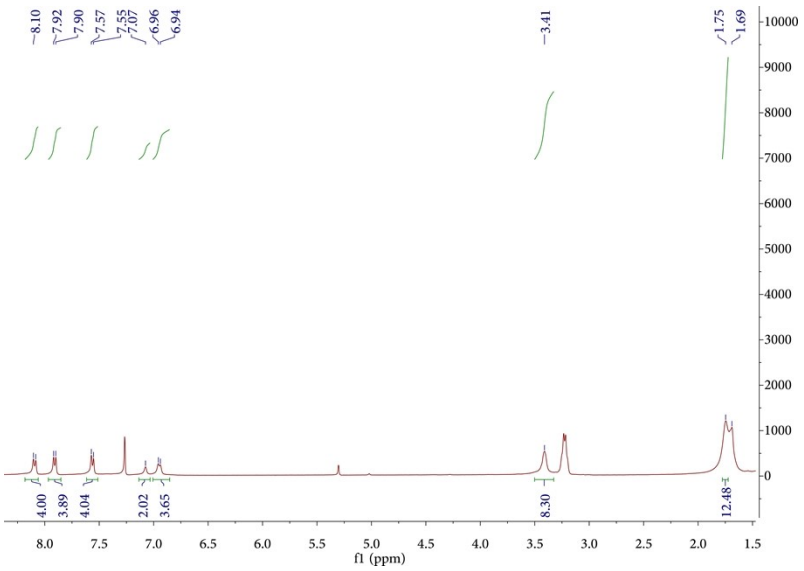


Fig. S6 The ^{1}H NMR spectrum of **Probe 1** in $CDCl_3$.

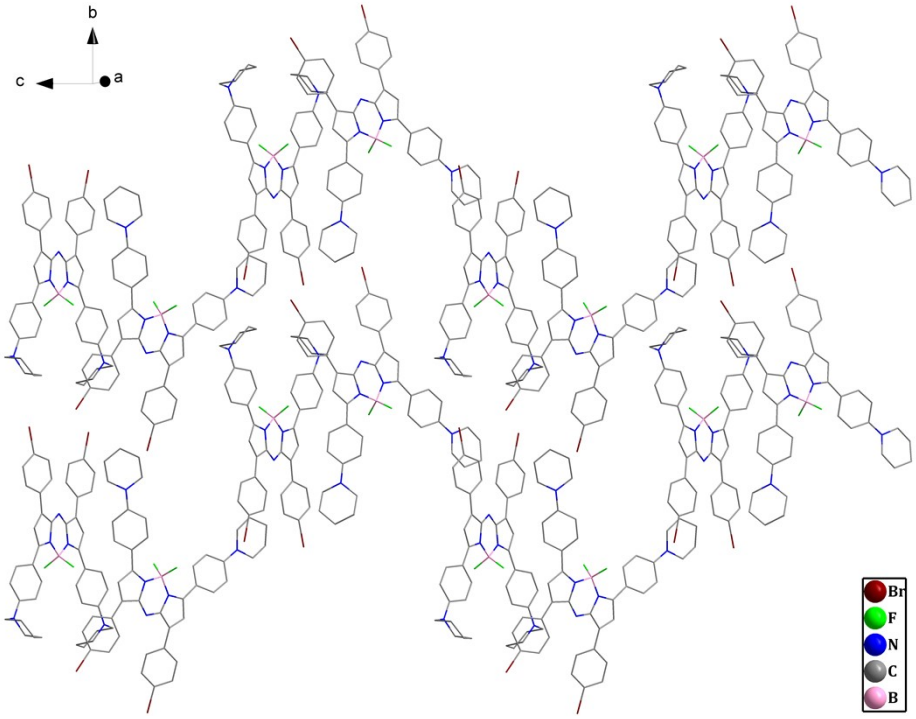


Fig. S7 X-Ray Structure of Probe 1-packing. All hydrogens and CH_2Cl_2 solvent are omitted for clarity.

Table S1. Crystallographic data for Probe 1

Complex	Probe 1
Empirical formula	$C_{128}H_{116}B_3Br_6Cl_4F_6N_{15}$
Formula weight	2632.04
Crystal system	Monoclinic
Space group	*C 2/c*
a (Å)	21.709(3)
b (Å)	18.350(3)
c (Å)	30.119(4)
α (°)	90
β (°)	105.139(2)
γ (°)	90
V (Å^3)	11582(3)
Z	4
D_c (g·cm^{-3})	1.509
μ (mm^{-1})	2.241
F (000)	5344
Crystal size (mm^3)	0.13 x 0.11 x 0.09 mm
θ Range	1.401 to 25.009
Reflections collected	41450
Independent reflections	10183 [R(int) = 0.0907]
Reflections observed [$I > 2\sigma(I)$]	5076
Data/restraints/parameters	10183/12/731
Goodness-of-fit on F^2	0.978
R_1/wR_2 [$I > 2\sigma(I)$]	0.0684/0.1701
R_1/wR_2 (all data)	0.1555/0.1971
Max., Min. Δ*ρ* (e·Å^{-3})	0.647, -0.576

Table S2. Selected bond lengths (Å) and angles (°) for Probe 1

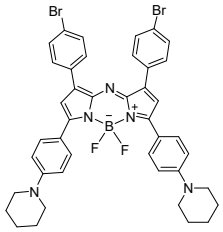
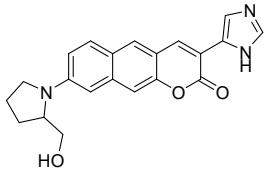
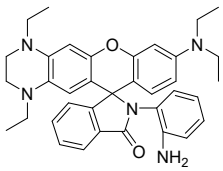
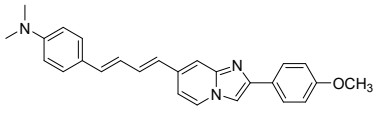
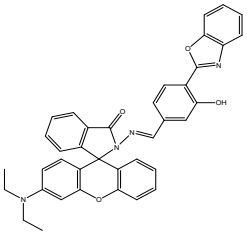
Selected bond lengths (Å)		Selected angles (°)	
B1-F1	1.393(7)	F1-B1-F2	110.5(5)
B1-F2	1.367(7)	C1-N1-C5	119.6(5)
B1-N2	1.568(8)	C(24)-N(4)-C(27)	117.9(5)
B1-N3	1.556(7)	C(24)-N(4)-C(31)	119.1(5)
Br1-C9	1.903(6)	C(35)-N(5)-C(42)	120.5(6)
Br2-C15	1.884(6)	C(35)-N(5)-C(38)	119.6(5)
N4-C24	1.390(7)	C(16)-C(15)-Br(2)	119.7(5)
N4-C27	1.447(8)	C(14)-C(9)-Br(1)	120.2(5)
N4-C31	1.448(7)		
N5-C35	1.393(7)		
N5-C38	1.415(8)		
N5-C42	1.395(8)		

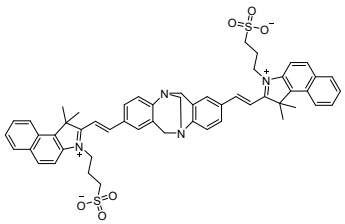
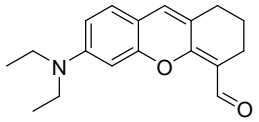
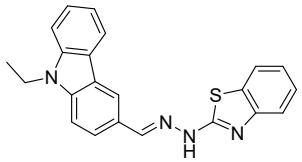
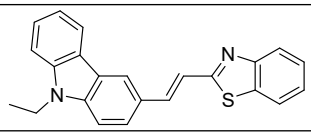
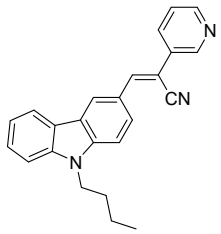
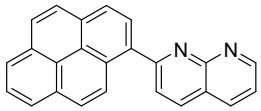
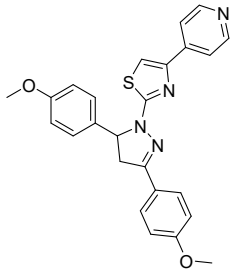
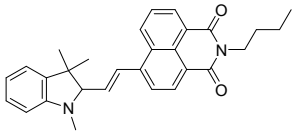
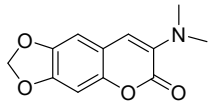
Table S3. Spectroscopic data of BDP and Probe 1 in different solvents

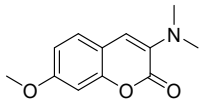
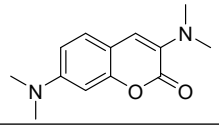
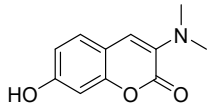
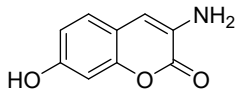
Compound	Solvent	Absorption	Emission		Ref.
		λ_{max} [nm](logε[$M^{-1}cm^{-1}$])	λ_{max} [nm]	Φ_{PL}	
BDP	DCM	655 (4.93)	692	15%	1
Probe 1	Toluene	554 (4.02), 804 (4.36)	n.d.[a]	–	This work
	DCM	562 (4.01), 811 (4.30)	n.d.	–	This work
	CH_3CN	562 (3.91), 811 (4.28)	n.d.	–	This work
	THF	559 (4.02), 814 (4.34)	n.d.	–	This work

[a] No emission was detected.

Table S4. Comparison of Probe 1 with the reported colorimetric and fluorescent extreme acidity probes

Ref.	Probe	Absorbance (nm)	Emission (nm)	Type of probe	pK_a	pH range
This work		811	686	turn-on	2.17	0.84-3.15
2		425	555	ratiometric	1.3	1.0-4.0
3		361	450	ratiometric	2.9	2.0-4.0
4		412	650	ratiometric	3.1	2.5-4.1
5		325	593	ratiometric	–	2.9-5.0

6		457	586	turn-on	1.79	0.10-3.24
7	CD-A	502	512	turn-on	2.90	1.5-4.0
	CD-B	502	511	turn-on	2.63	1.0-4.0
8	AuNC	300	670	turn-on	3.41	2.4-4.6
9		490	580	ratiometric	3.11	2.0-4.0
10		370	424	turn-on	2.73	2.21-3.30
11		453	583	ratiometric	1.62	1.0-3.3
12		391	502	turn-off	2.93	2.6-3.3
13		368	515	turn-off	2.98	1.6-6.7
14		350	460	turn-off	3.52	2.0-7.0
15		360	430	turn-on	1.6	1.0-3.0
16		361	450	turn-on	2.9	1.8-7.7

	334	406	turn-on	3.0	1.8-7.6
	406	526	turn-on	4.3	1.9-7.7
	334	465	turn-on	3.2	1.8-7.6
	332	465	turn-on	2.1	1.7-7.7

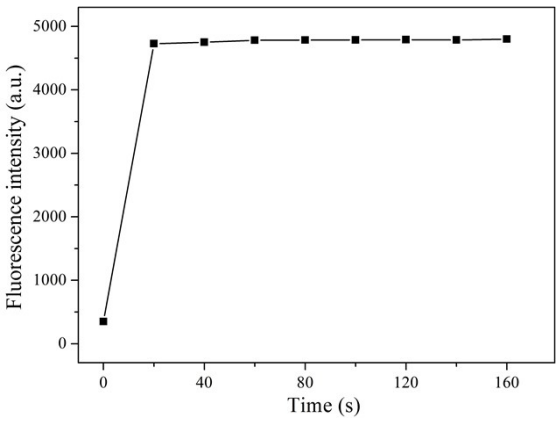


Fig. S8 The response time of Probe 1 towards H^+ ($[H^+]$ = 0.10 mol/L).

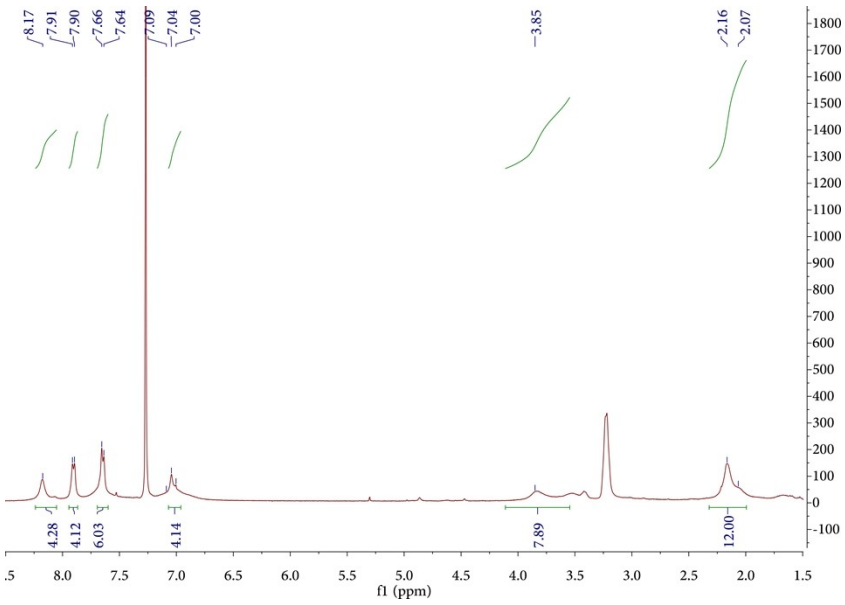
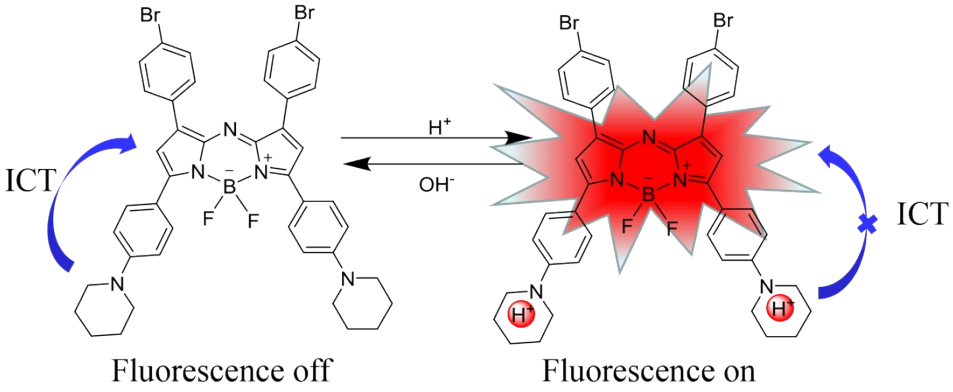


Fig. S9 The ^1H NMR spectrum of Probe 1 in $CDCl_3$ after the addition of excess of TFA.



Scheme S1 The proposed sensing mechanism of Probe 1 toward pH.

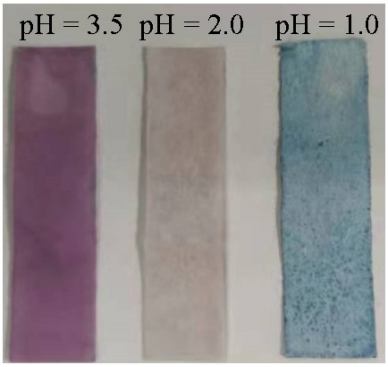


Fig. S10 Colour changes of test papers based on Probe 1 at different pH values.

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