Supplementary Material (ESI) for Chemical Communications

Supporting Information

Superimposed molecular keypad lock and half-subtractor implications in a single fluorophore

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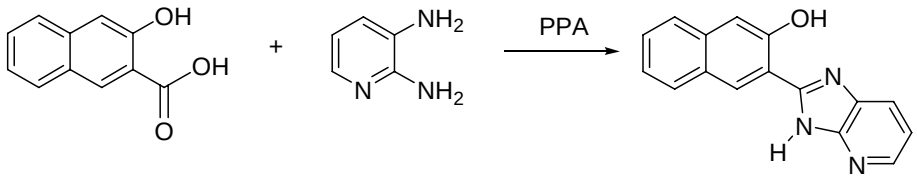
1. **General Experiment Conditions:** ^{1}H NMR Spectra and titrations were carried out at temperature 25 ^{o}C using JEOL A1 spectrometer operating at 300 MHz. ^{13}C NMR sepctra were recorded at 75 MHz. All chemical shifts are reported in ppm relative to the TMS as an internal reference. UV-Vis studies were carried out on a Shimadzu UV-1601 PC or Shimadzu UV-2400 machines using slit width of 1.0 nm and matched quartz cells. The fluorescence experiments were performed on Shimadzu 1501 fluorescence spectrophotometer. Elemental analysis were performed on Flash EA-1112 series CHNS-O analyser instrument.

2. Synthesis of fluorophore 2



2

A mixture of 2,3-diaminopyridine (1 mmol) and 3-hydroxy-2-naphthoic acid (1 mmol) in PPA (polyphosphoric acid) was heated at 140 ^{o}C for 6 hrs. The reaction mixture was poured into ice, neutralised with NH_4OH and filtered and then dried to get brown colored solid which was further re-crystallized from $CHCl_3$: MeOH mixture to get pure **2**, mp. 180 ^{o}C, 80%, FAB Mass M^+ m/z = 262 (M^++1); ^{1}H NMR (DMSO-d_6, 300 MHz) : δ 7.27-7.36 (m, 3H, 3 ArH), 7.47 (t, J = 6.9 Hz, 1H, ArH), 7.72 (d, J = 6.9 Hz, 1H, ArH), 7.85 (d, J = 6.9 Hz, 1H, ArH), 8.04 (d, J = 6.9 Hz, 1H, ArH, observed on addition of TBAF), 8.42 (bs, 1H, ArH), 8.79 (s, 1H, ArH). ^{13}C NMR (DMSO-d_6, 75 MHz): 110.9, 114.7, 118.8, 123.9, 124.3, 126.0, 127.0, 128.1, 128.5, 128.6, 130.0, 135.7, 143.3, 149.6, 153.2, 154.4. Elemental analysis: Found: C, 73.23; H, 4.29; N, 16.02%. $C_{16}H_{11}N_3O$ requires C, 73.55; H, 4.24; N, 16.08; O, 6.12%.

3. Photophysical studies – Parameters and Conditions

All the UV-Vis and Fluorescence studies have been performed in CH_3CN. All absorption scans and fluorescence spectra were saved as ACS II files and further processed in Excel™ to produce all graphs shown. Solutions of **2** were typically 20 µM for UV-Vis studies and 1 µM for fluorescence studies.

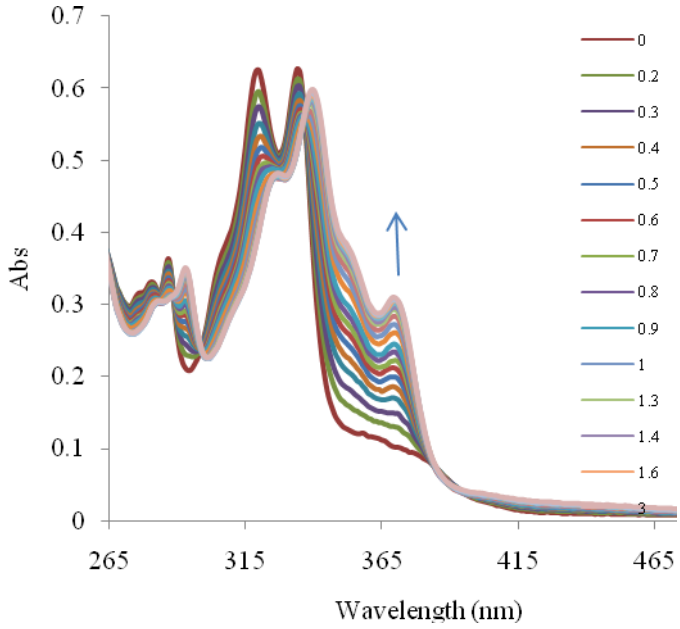


Figure SI-1: Effect of incremental addition of fluoride ions on the UV-Vis Spectrum of **2** (20 µM, CH_3CN)

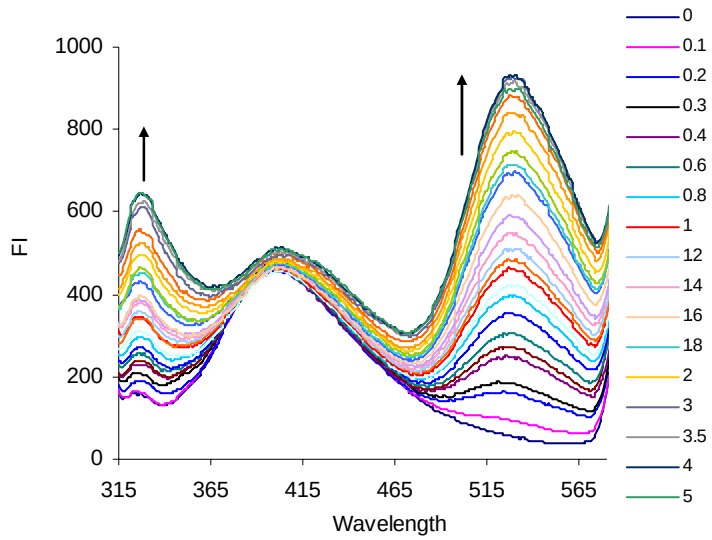


Figure SI-2: Effect of incremental addition (equivalents) of fluoride ions on the fluorescence spectrum of **2** (1µM, CH_3CN)

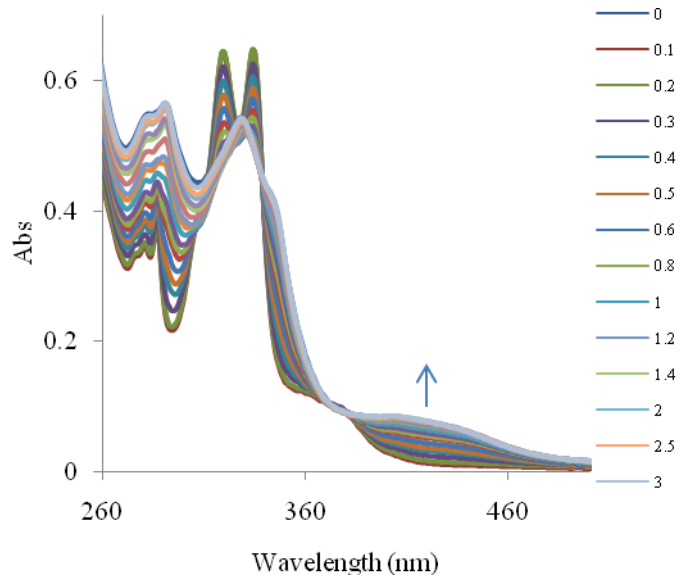


Figure SI-3: Effect of incremental addition (equivalents) of Cu^{2+} on UV-Vis spectrum of **2** (20 µM, CH_3CN).

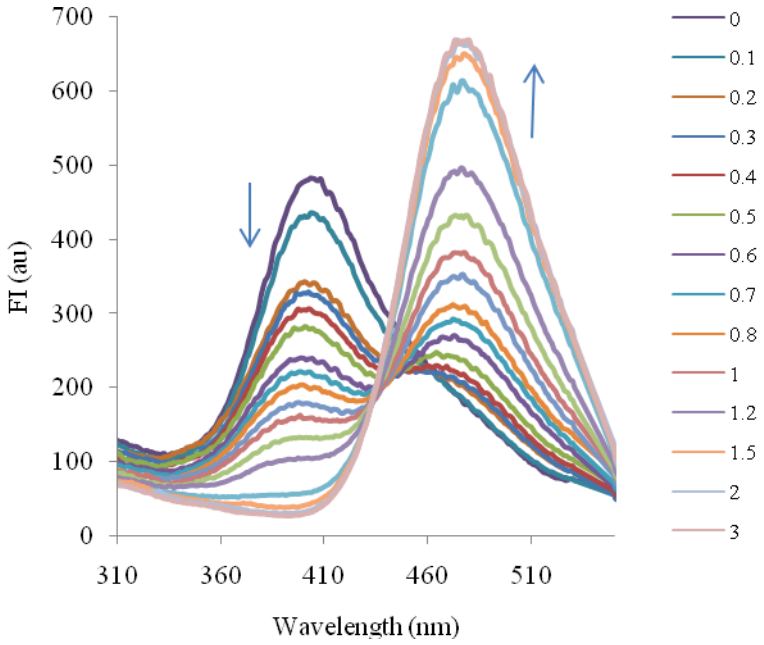


Figure SI-4: Effect of incremental addition (equivalents) of Cu^{2+} on fluorescence spectrum of **2** (1µM, CH_3CN)

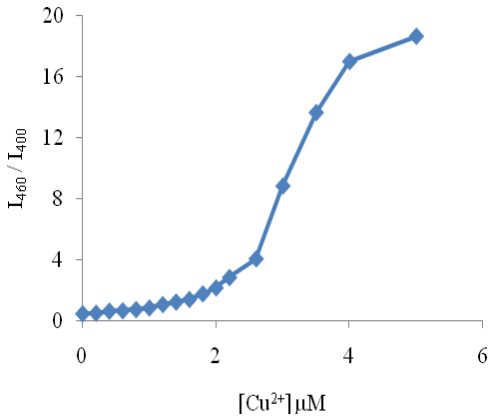


Figure SI-5: Ratiometric plot for estimation of Cu^{2+} using fluorophore 2

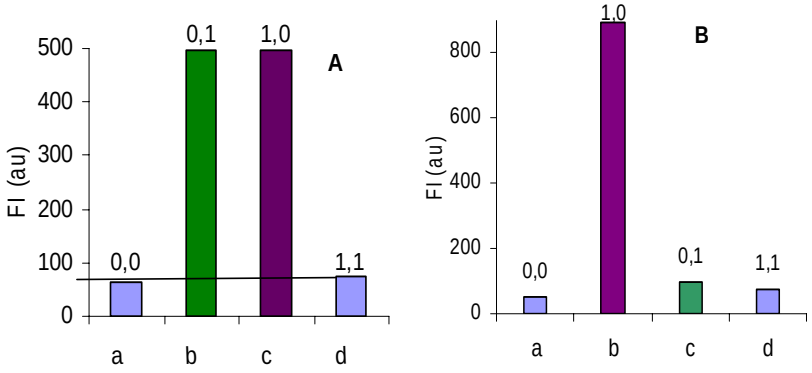


Figure SI-6: Bar diagram of half-subtractor showing the fluorescence intensities with different inputs;.a only **2**; b, **2** + TBA F (2 µM); c, **2**+ Cu^{2+} (2 µM); d, **2** + TBA F (2 µM) + Cu^{2+} (2 µM) ('A' is XOR at 490 nm ; 'B' is INHIBIT at 540 nm)

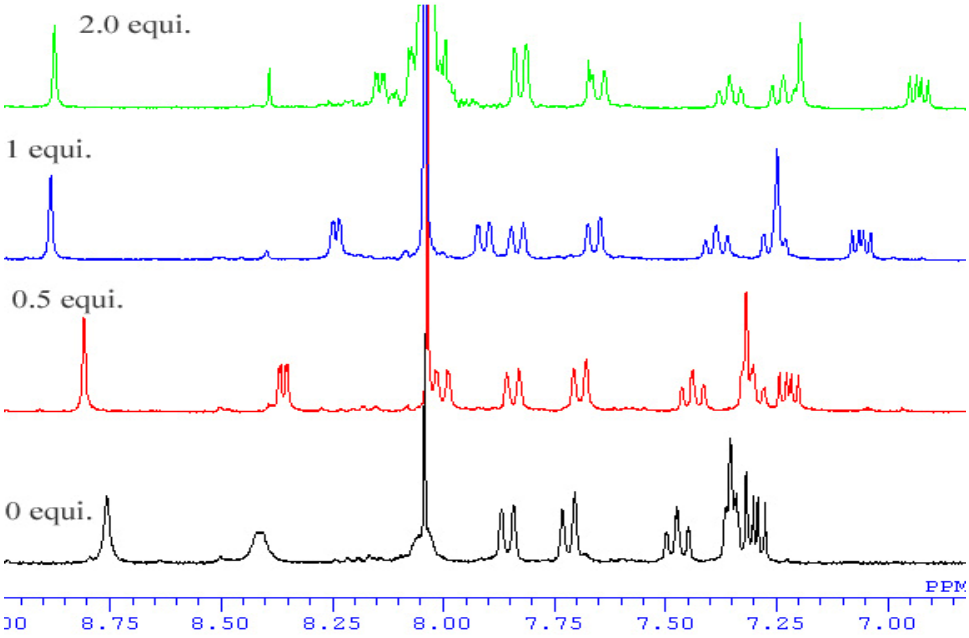
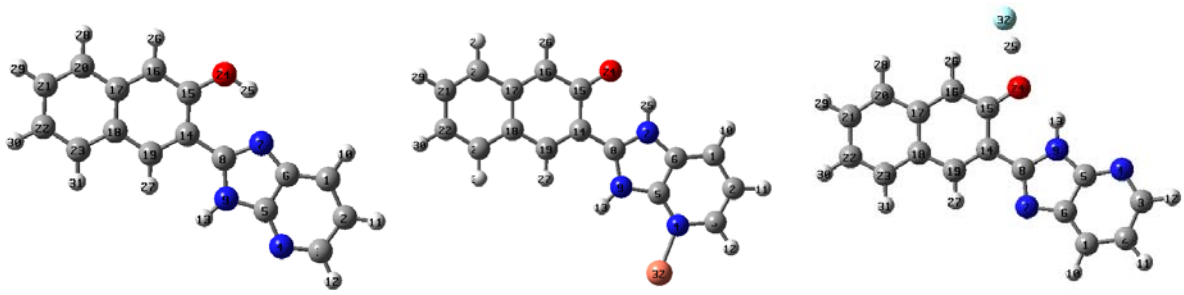


Figure SI-7: Effect of incremental addition of TBA F on ^{1}H NMR spectra of probe **2**

Density functional theory Calculations

All calculations were performed with Gaussian 98 (G98) suite of programme. Calculations were performed using Density functional theory (DFT) with Becke`s three parameter hybrid exchange functional and Lee-Yang-Parr correlation functional (B3LYP). The double – basis set of Hay and Wadt (LANL2DZ) was used for the copper center. The ligand hydrogen, carbon, nitrogen and oxygen were described using the 6-31G* basis set.



Probe 2 **Probe 2-Cu^{2+} complex** **Probe 2-F^- complex**

Table: The bond lengths, bond angles and Mulliken charges in gas phase optimized structures of probe **2**, Probe **2**-Cu^{2+} and Probe **2** –F^- complexes

PARAMETERS	Probe 2	Probe 2 -Cu^{2+} complex	Probe 2 - F^- complex
BOND LENGTHS(Å)			
C2-C1	1.394	1.408	1.397
C3-C2	1.406	1.404	1.404
N4-C3	1.341	1.380	1.343
C5-N4	1.326	1.354	1.330
C6-C1	1.395	1.399	1.396
N7-C6	1.379	1.393	1.373
C8-N7	1.329	1.362	1.334
N9-C8	1.378	1.389	1.377
H10-C1	1.085	1.085	1.087
H11-C2	1.085	1.084	1.087
H12-C3	1.087	1.084	1.089
H13-N9	1.008	1.012	1.029
C8-C14	1.457	1.440	1.458

C15-C14	1.443	1.486	1.462
C16-C15	1.384	1.440	1.409
C17-C16	1.411	1.409	1.403
C18-C17	1.435	1.453	1.442
C19-C14	1.388	1.396	1.386
C20-C17	1.423	1.431	1.429
C21-C20	1.375	1.398	1.375
C22-C21	1.419	1.420	1.421
C23-C18	1.423	1.417	1.420
O24-C15	1.345	1.293	1.301
H25-O24	0.993	1.713	1.512
H26-C16	1.085	1.087	1.086
H27-C19	1.087	1.090	1.087
H28-C20	1.087	1.086	1.088
H29-C20	1.086	1.085	1.088
H30-C22	1.086	1.085	1.087
H31-C23	1.087	1.087	1.089
	---	1.941(Cu32-N4)	0.990 (F32-H25)
H25-N7	1.841	1.028	
BOND ANGLES(^{O})			
C3-C2-C1	120.5	120.8	120.2
N4-C3-C2	124.4	122.9	124.6
C5-N4-C3	113.5	116.1	113.8
C6-C1-C2	116.3	116.0	116.9
N7-C6-C1	132.7	133.0	132.1
C8-N7-C6	106.1	110.5	104.4
N9-C8-N7	111.4	107.2	112.9
H10-C1-C2	122.1	121.6	121.9

H11-C2-C1	120.3	120.5	120.5
H12-C3-C2	119.7	120.0	119.6
H13-N9-C5	124.8	126.4	134.2
H14-C8-N7	124.6	129.3	120.7
C15-C14-C8	119.4	117.0	120.4
C16-C15-C14	119.3	117.8	116.6
C17-C16-C15	121.8	121.9	122.7
C18-C17-C16	119.2	119.4	119.8
C19-C14-C15	118.9	119.4	120.6
C20-C17-C16	122.4	121.5	122.5
C21-C20-C17	120.8	120.3	121.3
C22-C21-C20	120.7	120.3	120.7
C23-C18-C19	122.3	121.4	122.5
O24-C15-C14	122.3	121.4	121.2
H25-O24-C15	108.6	108.6	111.7
H26-C16-C17	120.2	121.4	120.6
H27-C19-C18	117.4	116.8	119.7
H28-C20-C17	118.6	119.3	118.2
H29-C21-C20	119.8	120.0	119.8
H30-C22-C21	119.7	119.5	119.9
H31-C23-C22	120.4	119.5	120.4
Cu32-N4-C3	---	116.1	173.9

Mulliken Charges

S. No.	ATOM	**Probe 2**	**Probe 2 - Cu^{2+} complex**	**Probe 2 - F^- complex**
1	C	-0.130942	-0.251467	-0.160118
2	C	-0.165030	-0.107552	-0.166344
3	C	0.028965	-0.127977	0.013250
4	N	-0.508175	-0.361671	-0.513254

5	C	0.507706	0.224474	0.515342
6	C	0.290127	0.294842	0.262674
7	N	-0.693862	-0.400002	-0.612292
8	C	0.561424	0.296978	0.471533
9	N	-0.739881	-0.418650	-0.726952
10	H	0.155376	0.305893	0.116510
11	H	0.140777	0.288702	0.096824
12	H	0.144417	0.263740	0.102370
13	H	0.348602	0.371634	0.378298
14	C	0.107905	0.283535	0.040963
15	C	0.310878	0.101200	0.410726
16	C	-0.261851	-0.473832	-0.349559
17	C	0.153325	0.428458	0.171361
18	C	0.141828	0.414336	0.131375
19	C	-0.293009	-0.499082	-0.291986
20	C	-0.195585	-0.336006	-0.204824
21	C	-0.131815	-0.187987	-0.137489
22	C	-0.144096	-0.186094	-0.159557
23	C	-0.185589	-0.375365	-0.186914
24	O	-0.661477	-0.298625	-0.755958
25	H	0.440331	0.451275	0.475760
26	H	0.141179	0.302843	0.126893
27	H	0.114664	0.218818	0.135069
28	H	0.134230	0.282503	0.107638
29	H	0.132617	0.280417	0.089486
30	H	0.130576	0.276136	0.086563
31	H	0.126384	0.262031	0.100218
32		-----	0.676497(Cu)	-0.567607(F)