

SUPPORTING INFORMATION

An NIR emissive donor- π -acceptor dicyanomethylene-4H-pyran derivative as a fluorescent chemosensor system towards copper (II) detection

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NMR spectra

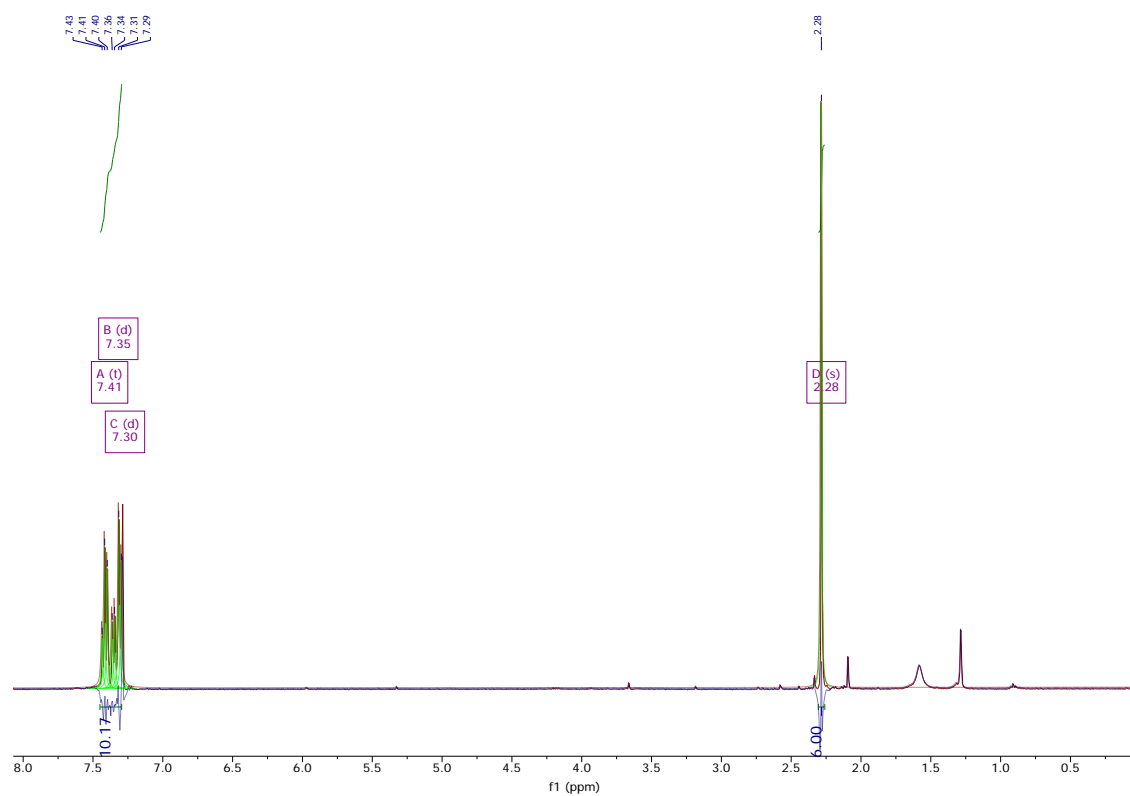


Figure S1. ¹H NMR spectrum of **1**.

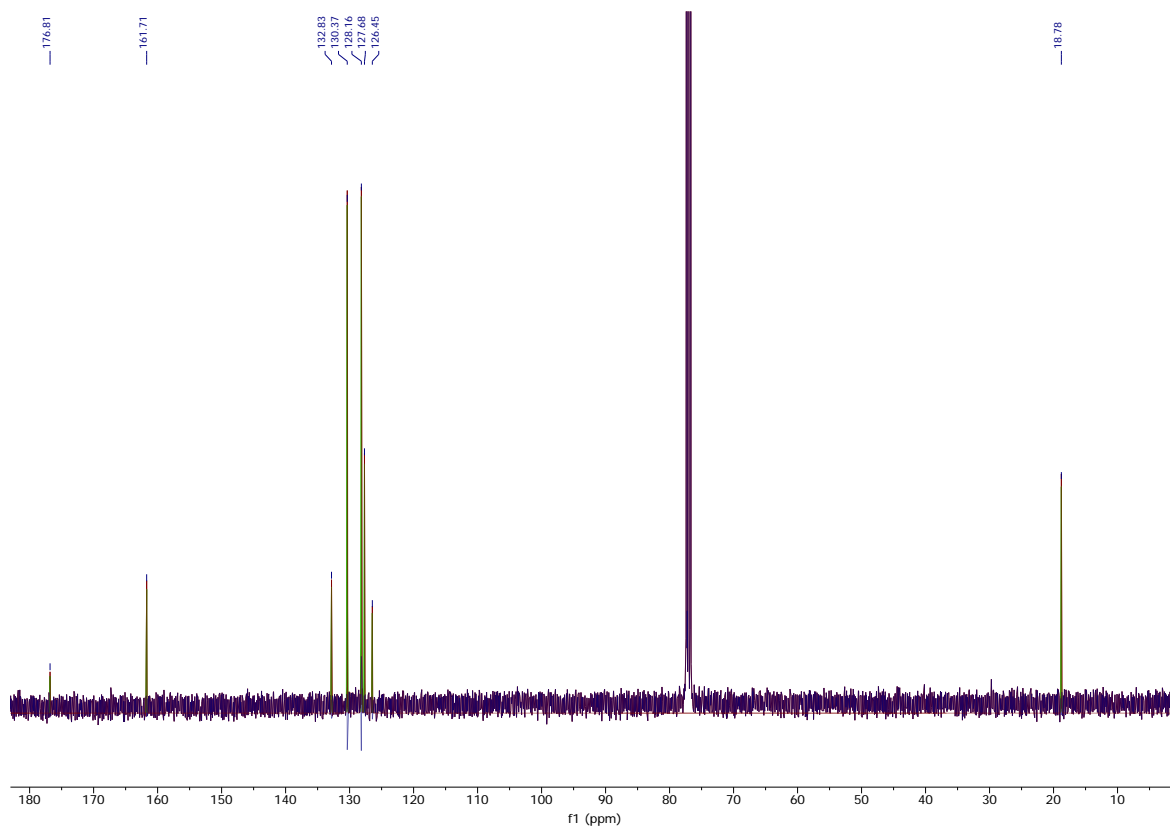


Figure S2. ¹³C NMR spectrum of **1**.

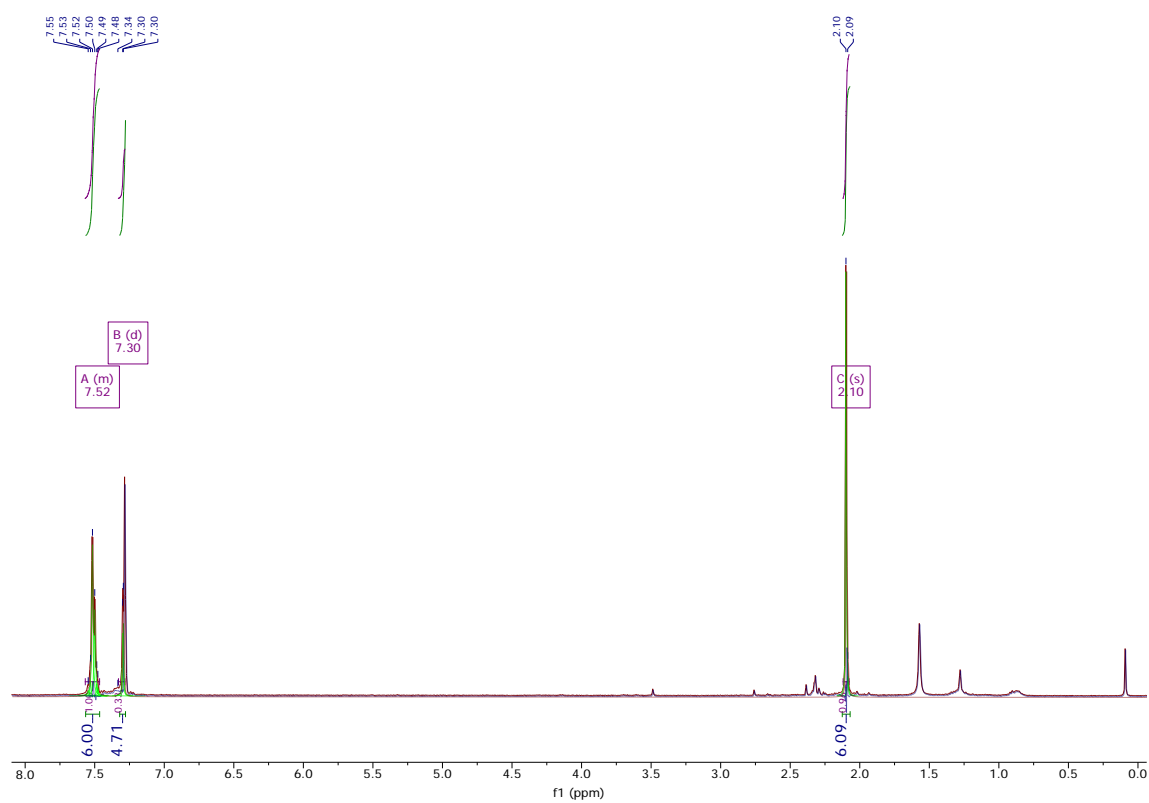


Figure S3. ¹H NMR spectrum of **2**.

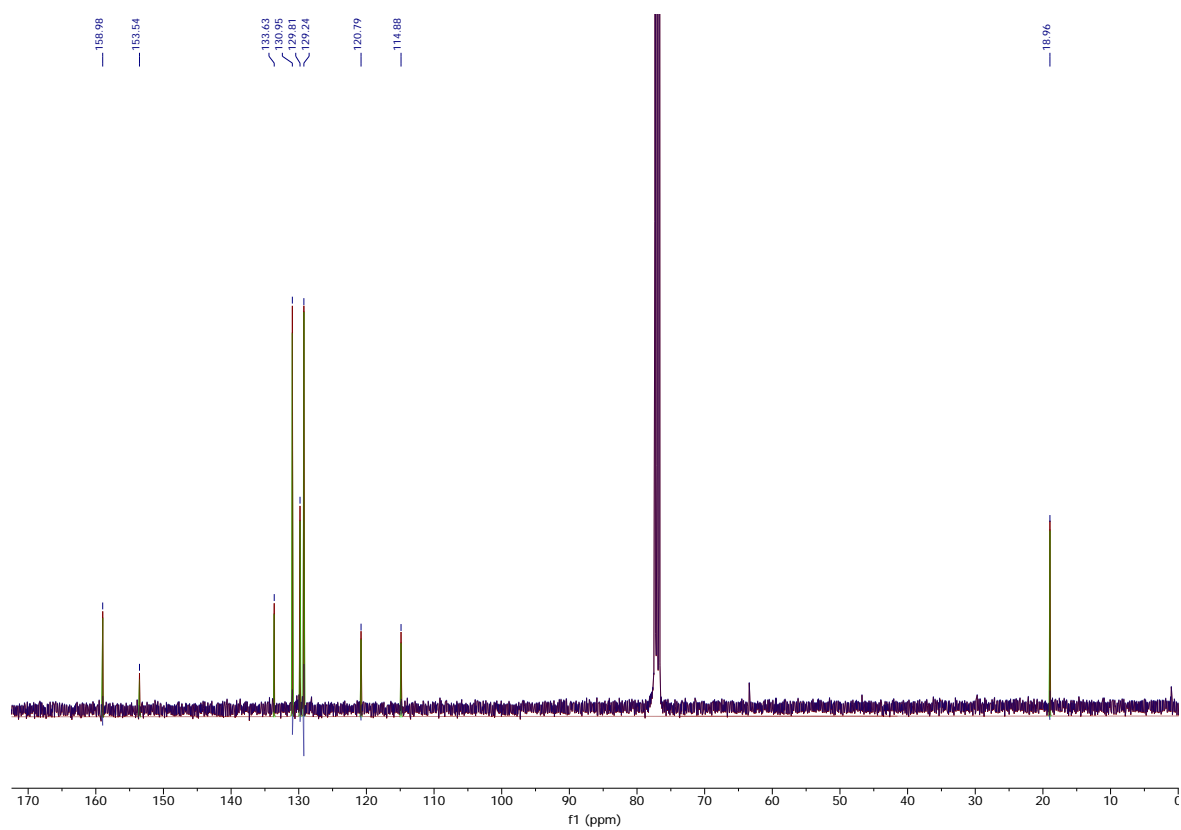


Figure S4. ¹³C NMR spectrum of **2**.



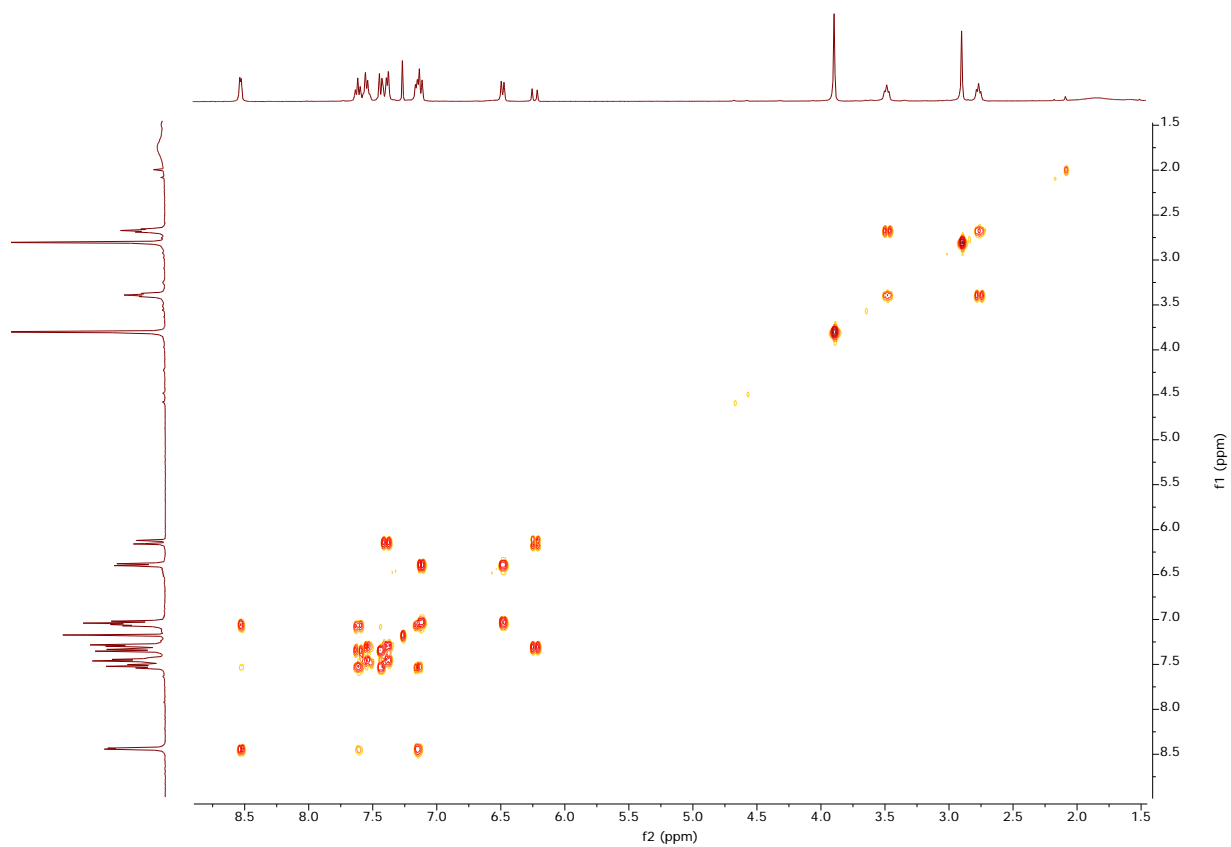


Figure S7. ^1H - ^1H COSY NMR spectrum of **4**.

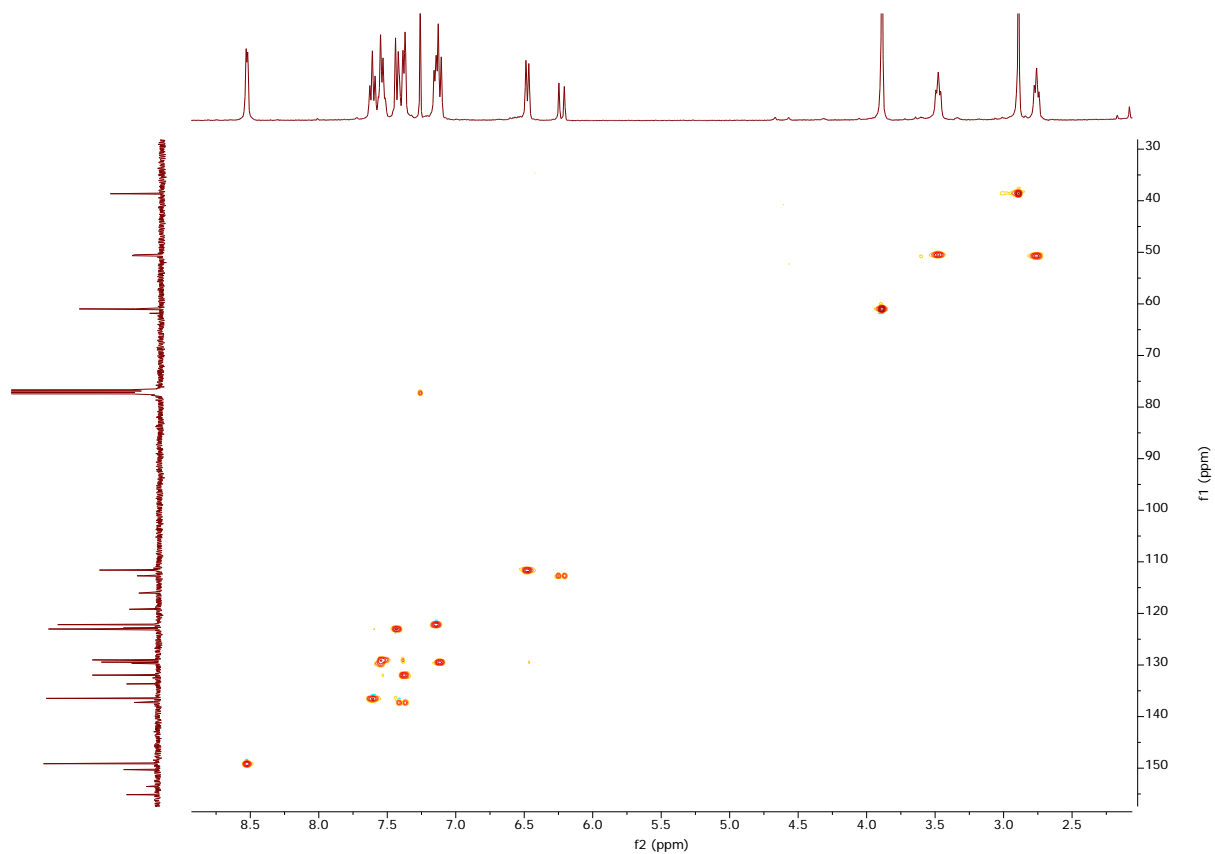


Figure S8. ^1H - ^{13}C HSQC NMR spectrum of **4**.

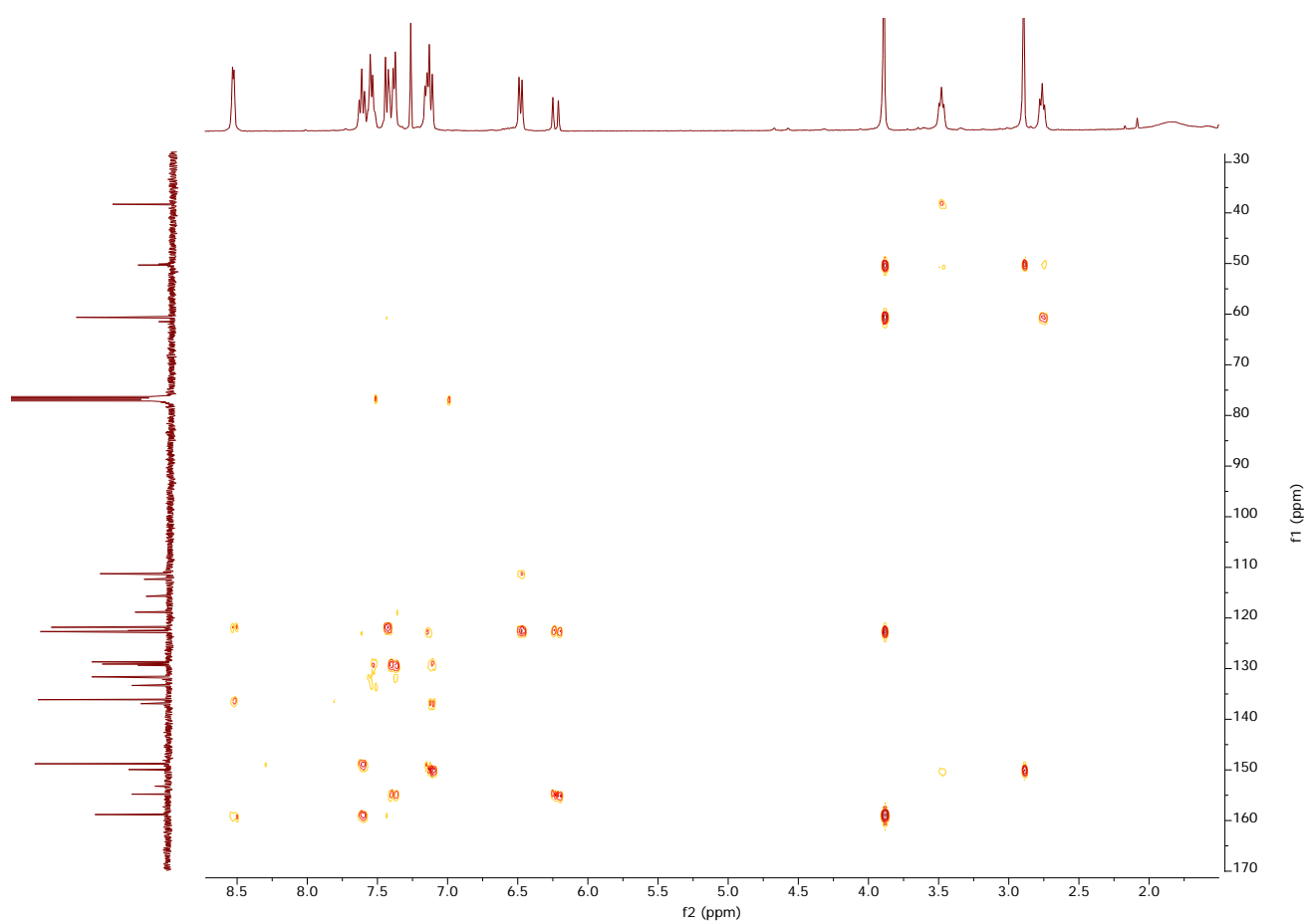


Figure S9. ^1H - ^{13}C HMBC NMR spectrum of **4**.

Table S1 – Full NMR peak assignment for chemosensor **4**.

Position	¹ H	¹³ C
1	-	116.06
2	-	153.56
3	-	119.20
4	-	133.67
5	7.38	131.96
6	7.53	129.01
7	7.55	129.67
8	7.53	129.01
9	7.38	131.96
10	-	122.97
11	6.22	112.71
12	7.39	137.26
13	-	155.13
14	7.12	129.44
15	6.48	111.60
16	-	150.27
17	6.48	111.60
18	7.12	129.44
19	2.89	38.64
20	3.48	50.65
21	2.76	50.47
22	3.89	60.97
23	-	159.16
24	8.53	149.15
25	7.15	122.17
26	7.61	136.47
27	7.43	123.02

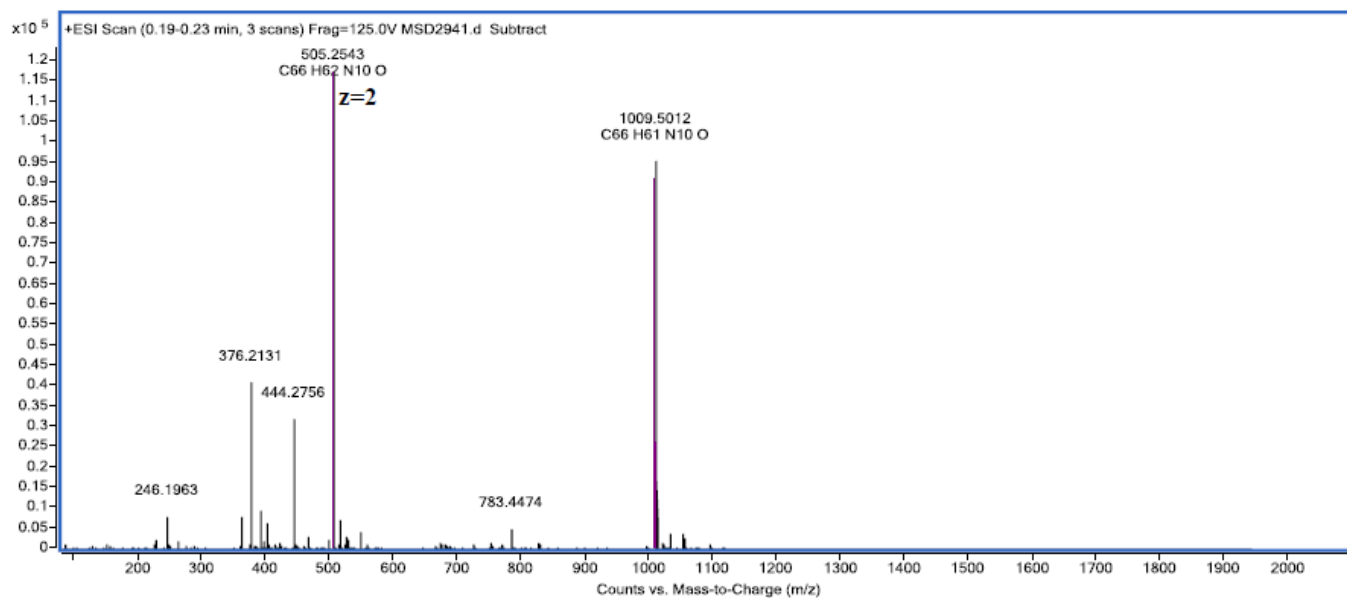


Figure S10. HRMS spectrum of **4**.

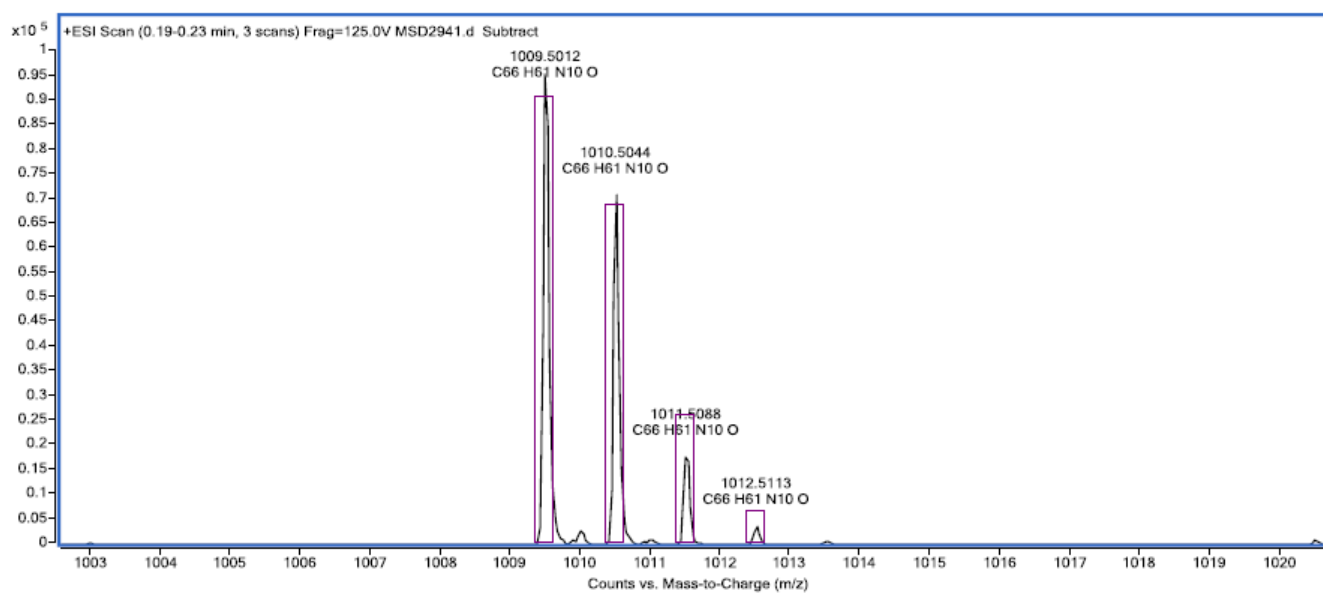


Figure S11. Zoom of the molecular ion peak from HRMS spectrum of **4**.

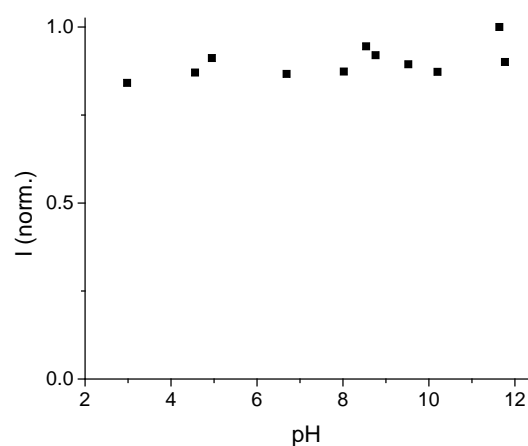


Figure S12. pH dependence of fluorescence emission of **4**, in a mixture of 50% MeOH (1.5mL) and 50% diluted Theorell and Stenhagen buffer [24] (0.5 mL buffer in 1.5 mL of water content). [**4**] = 2.5 μ M, λ_{exc} (**4**) = 500 nm.

Table S2 – Stokes shift from chemosensor **4** in different organic solvents, and their corresponding empiric polarity parameters.

Solvent	Stokes shift (cm^{-1})	E_T^N *
Toluene	4121	0.099
Diethylether	4383	0.117
Tetrahydrofuran	4905	0.207
Ethyl acetate	5000	0.228
Dichloromethane	5399	0.309
Acetonitrile	6734	0.46

*From reference 28.

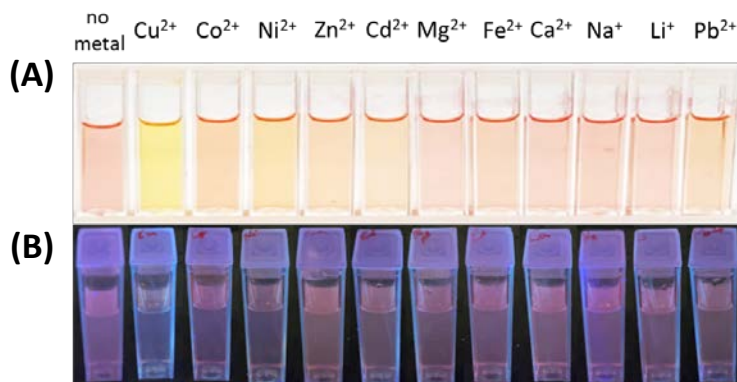


Figure S13. Naked-eye changes in chemosensor **4** (10 μ M), in a 50:50 mixture of methanol and 0.01M HEPES buffer at pH=7.1 (λ_{exc} = 500 nm), with different metal ions (2 equivalents): (A) on ambient light; (B) under UV light irradiation (365 nm).