Electronic Supplementary Material (ESI) for RSC Advances.

ELECTRONIC SUPPLEMENTARY INFORMATION

Novel fluorescent sensors based on benzimidazo[2,1-a]benz[de]isoquinoline-7-one-12-carboxylic acid fo Cu^{2+}

Zheng Liu, Yuhua Qi, Chaoxia Guo, Yingying Zhao, Xiaofeng Yang, Meishan Pei and Guangyou Zhang *

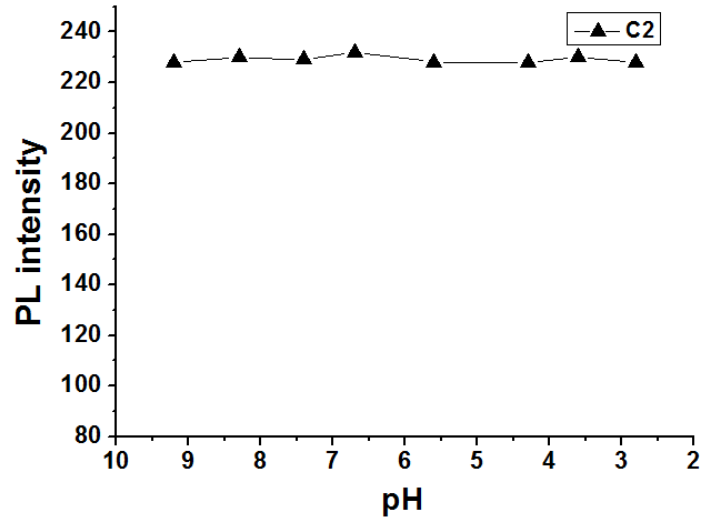


Figure S1. Emission intensity of **C2** versus the different pH values. Emission wavelength is at 510 nm.

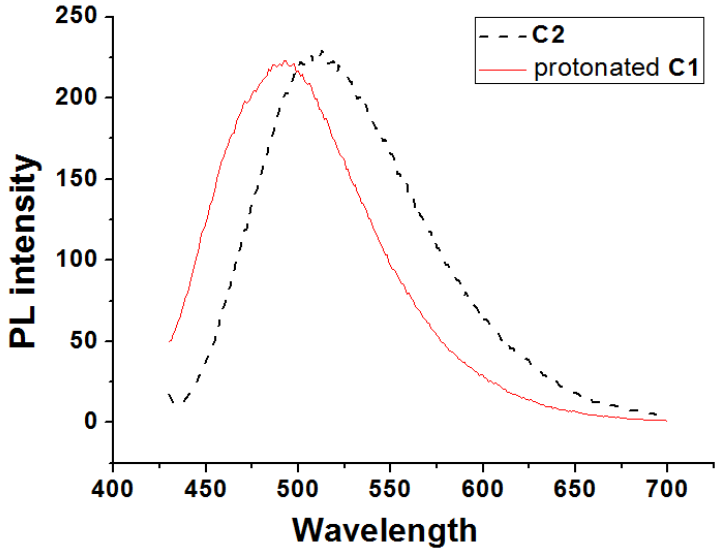


Figure S2. Emission spectra of protonated **C1** at pH 2.8 and that of **C2** in acetonitrile-H_20 (9:1) solution.

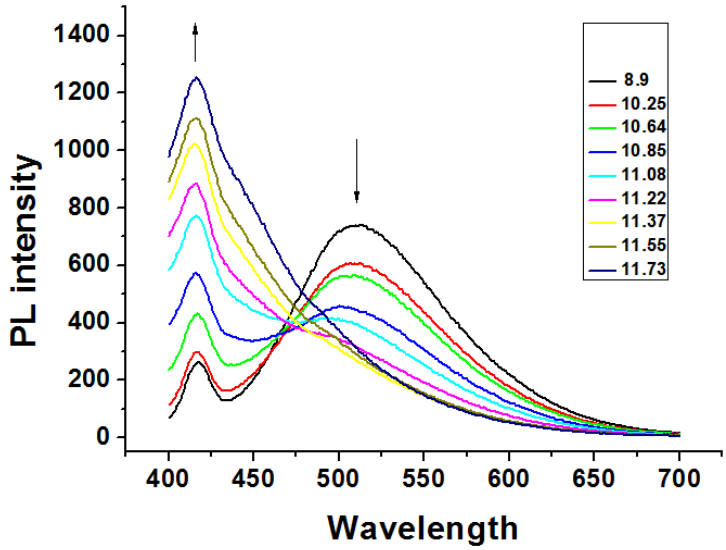


Figure S3. pH-dependence of the emission spectra of sensor **C2** (1×10^{-5}M) in pure water. The insert indicates the change of pH increases from 8.9 to 11.73 with the titration of NaOH. Excitation is at 370 nm.

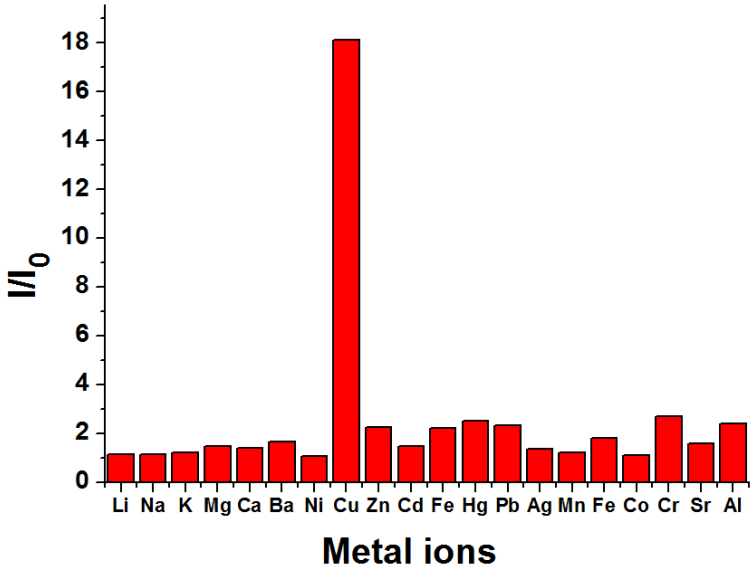


Figure S4. The relative PL intensity (I/I_0) of **C2** (1×10^{-5}M) in the presence of 20 equiv of Cu^{2+} (1×10^{-5}M) and 40 equiv of various other metal ions (Li^{+}, Na^{+}, K^{+}, Mg^{2+}, Ca^{2+}, Ba^{2+}, Ni^{2+}, Zn^{2+}, Cd^{2+}, Fe^{2+}, Hg^{2+}, Pb^{2+}, Ag^{+}, Mn^{2+}, Fe^{3+}, Co^{2+}, Cr^{3+}, Sr^{3+} and Al^{3+}) (1×10^{-5}M) in acetonitrile-H_20 (9:1) containing HEPES (5mM, pH=7.4) at 25 °C, respectively. Excitation is at 370 nm, and emission is monitored at 494 nm.

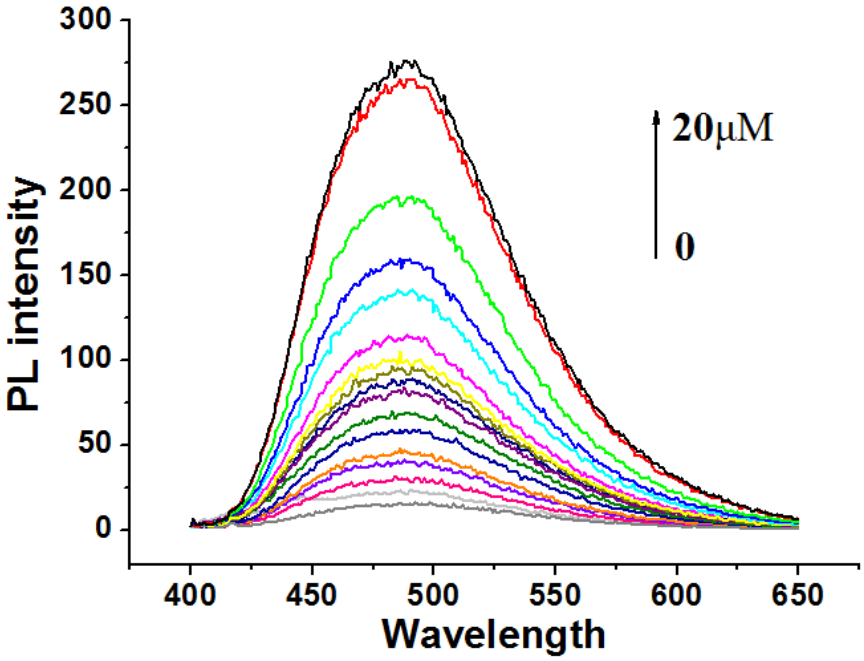


Figure S5. Changes in the PL intensity of **C2** (1×10^{-5}M) in acetonitrile-H_2O (9:1) containing HEPES (5mM, pH=7.4) upon titration with Cu^{2+} (1×10^{-5}M). Excitation is at 370 nm.

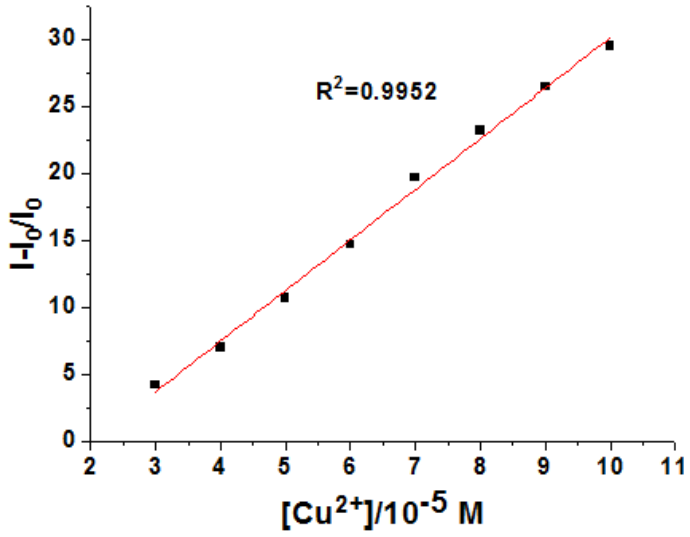


Figure S6. Change ratio of fluorescence of **C1** (1×10^{-5}M) upon addition of Cu^{2+} (1×10^{-5}M) in acetonitrile-H_20 (9:1) containing HEPES (5mM, pH=7.4) at 25 °C. Excitation is at 370 nm, and emission is monitored at 494 nm.

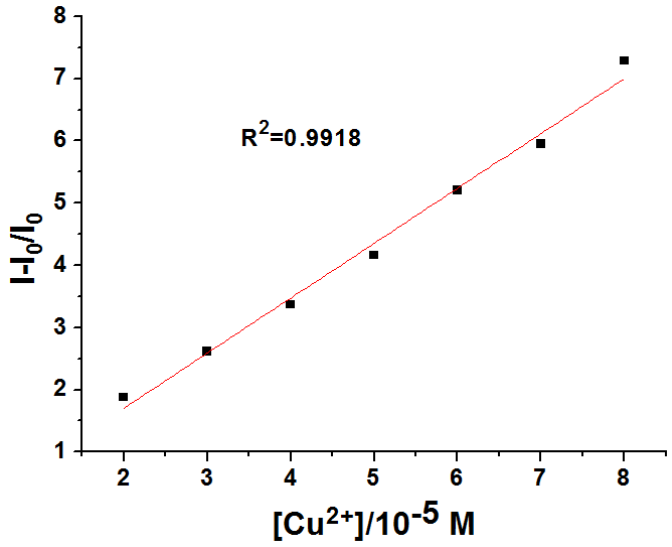


Figure S7. Change ratio of fluorescence of **C2** (1×10^{-5}M) upon addition of Cu^{2+} (1×10^{-5}M) in acetonitrile-H_20 (9:1) containing HEPES (5mM, pH=7.4) at 25 °C. Excitation is at 370 nm, and emission is monitored at 494 nm.

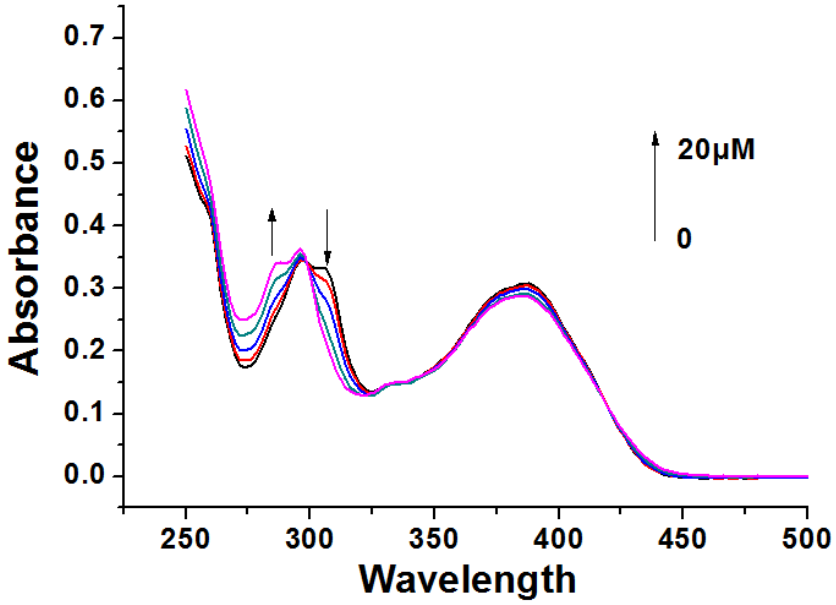


Figure S8. Changes in the absorption spectra of **C1** (1×10^{-5}M) in acetonitrile-H_2O (9:1) containing HEPES (5mM, pH=7.4) upon titration with Cu^{2+} (1×10^{-5}M). Excitation is at 370 nm.

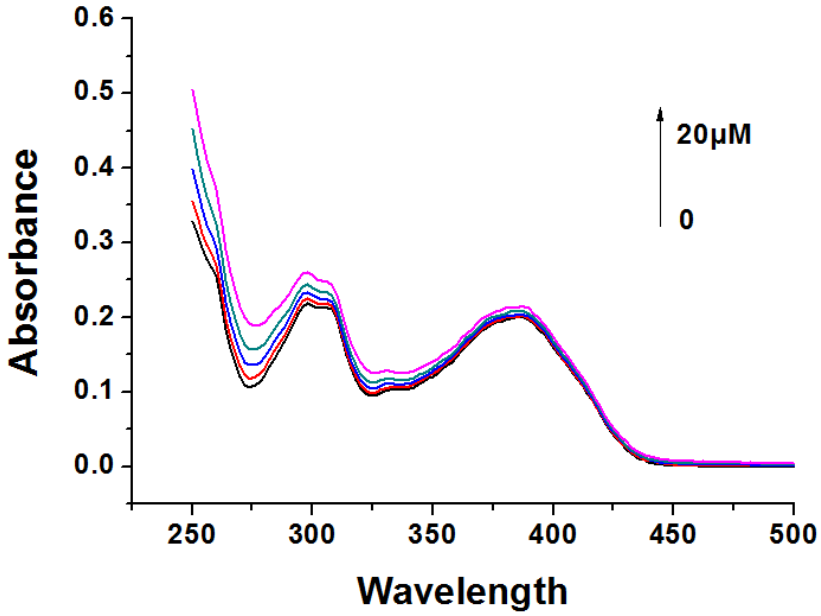


Figure S9. Changes in the absorption spectra of **C2** (1×10^{-5}M) in acetonitrile-H_2O (9:1) containing HEPES (5mM, pH=7.4) upon titration with Cu^{2+} (1×10^{-5}M). Excitation is at 370 nm.

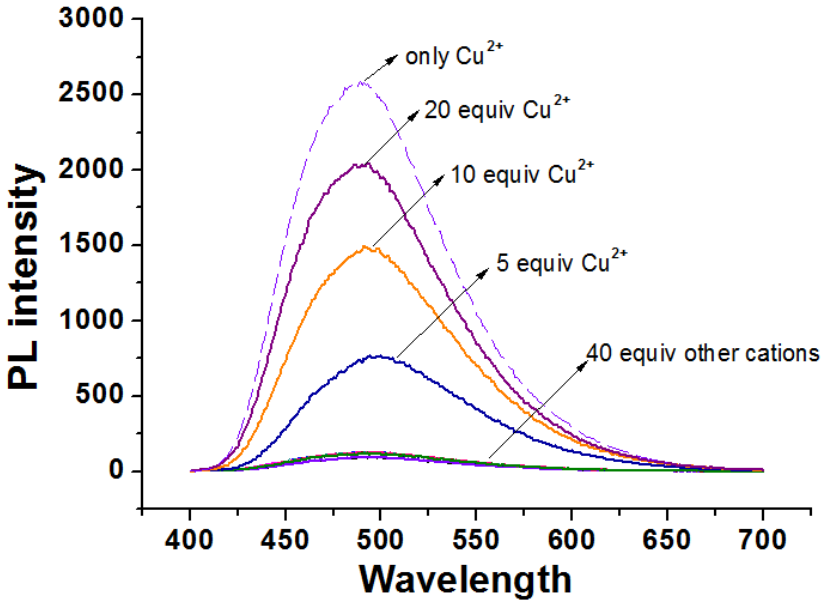


Figure S10. Competition experiments: fluorescence emission spectra of **C1** with addition of 40 equiv of (Li^+, Na^+, K^+, Mg^{2+}, Ca^{2+}, Ba^{2+}, Ni^{2+}, Zn^{2+}, Cd^{2+}, Fe^{2+}, Hg^{2+}, Pb^{2+}, Ag^+, Mn^{2+}, Fe^{3+}, Co^{2+}, Cr^{3+}, Sr^{3+} and Al^{3+}) (1×10^{-5}M) and Cu^{2+} (5equiv, 10 equiv, 20 equiv respectively) in acetonitrile-H_20

(9:1) containing HEPES (5mM, pH=7.4). Excitation is at 370 nm, and emission is monitored at 494 nm.

	orbital transition	E (eV)	λ (nm)	*f*
C2	HOMO-LUMO	3.0027	412.91	0.2226
C2+Cu^{2+}	HOMO(α)-LUMO(α) HOMO(β)-LUMO+1(β)	3.0816	402.33	0.3086

Table S1. Calculated excitation energy (E), wavelength (λ), and oscillator strength (f) for the lowest singlet electronic transition of C2 and doublet electronic transitions of **C1**+Cu^{2+} complex.

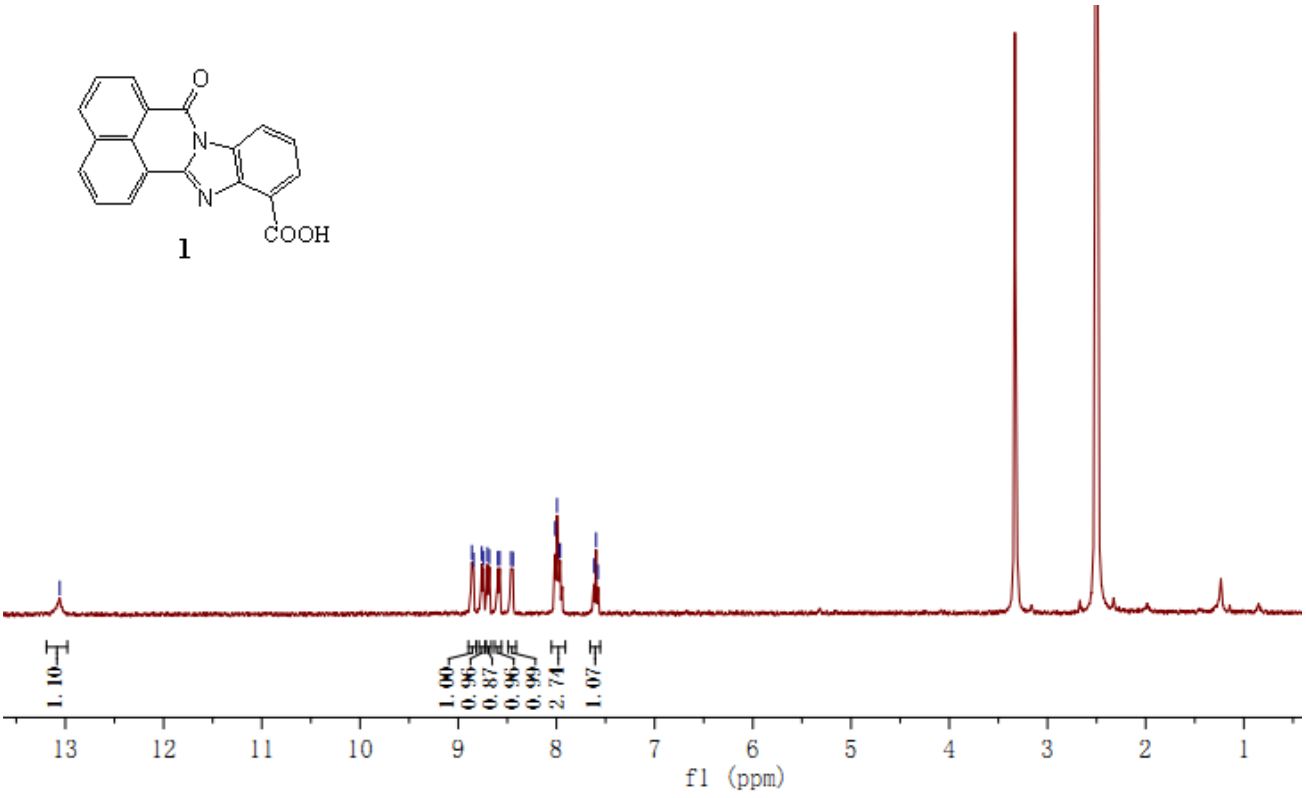


Figure S11. ^{1}H NMR spectrum of compound **1** (benzimidazo[2,1-a]benz[de]isoquinoline- 7-one-10-carboxylic acid) in $CDCl_3$.

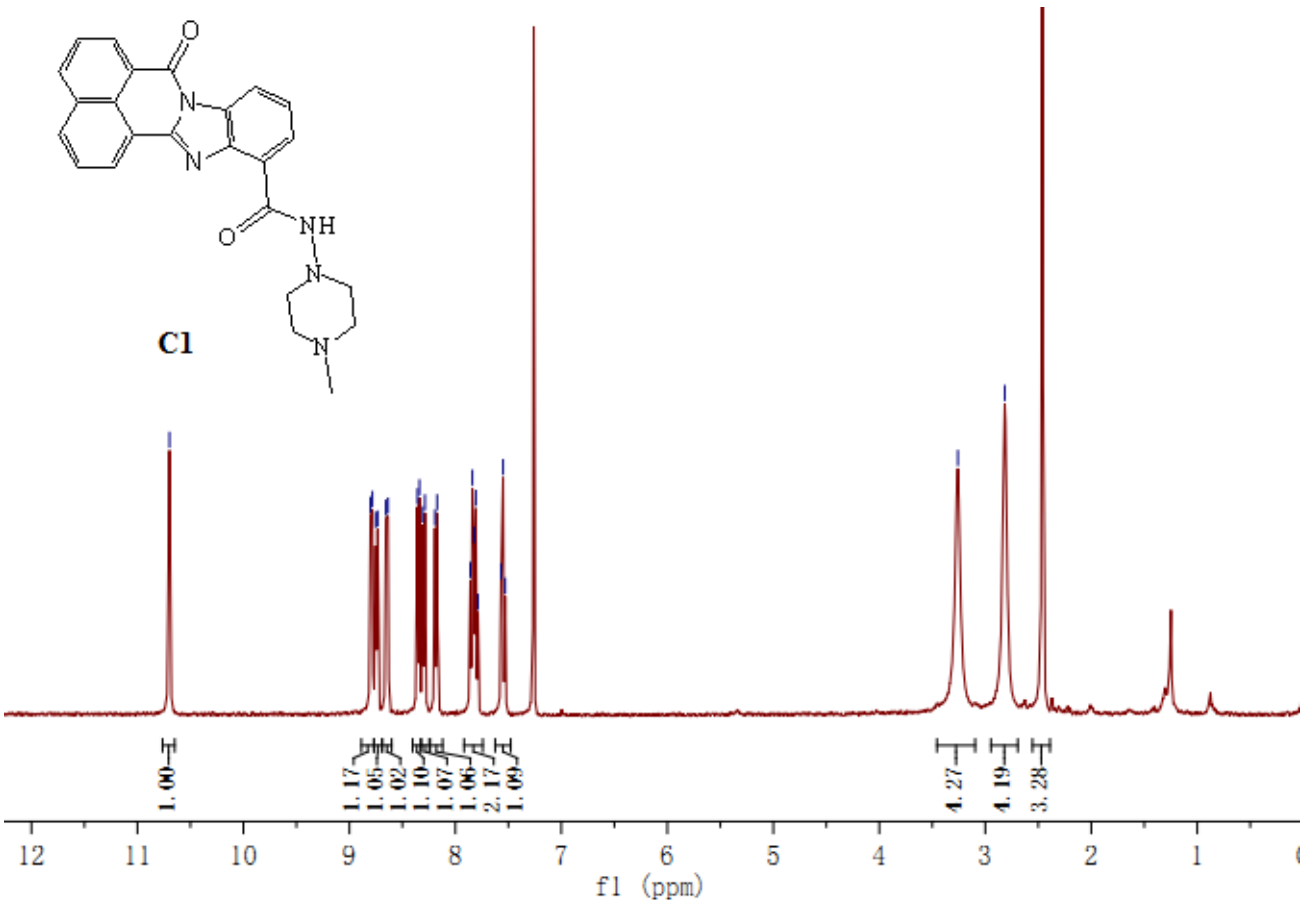


Figure S12. ^{1}H NMR spectra of **C1** in $CDCl_3$.

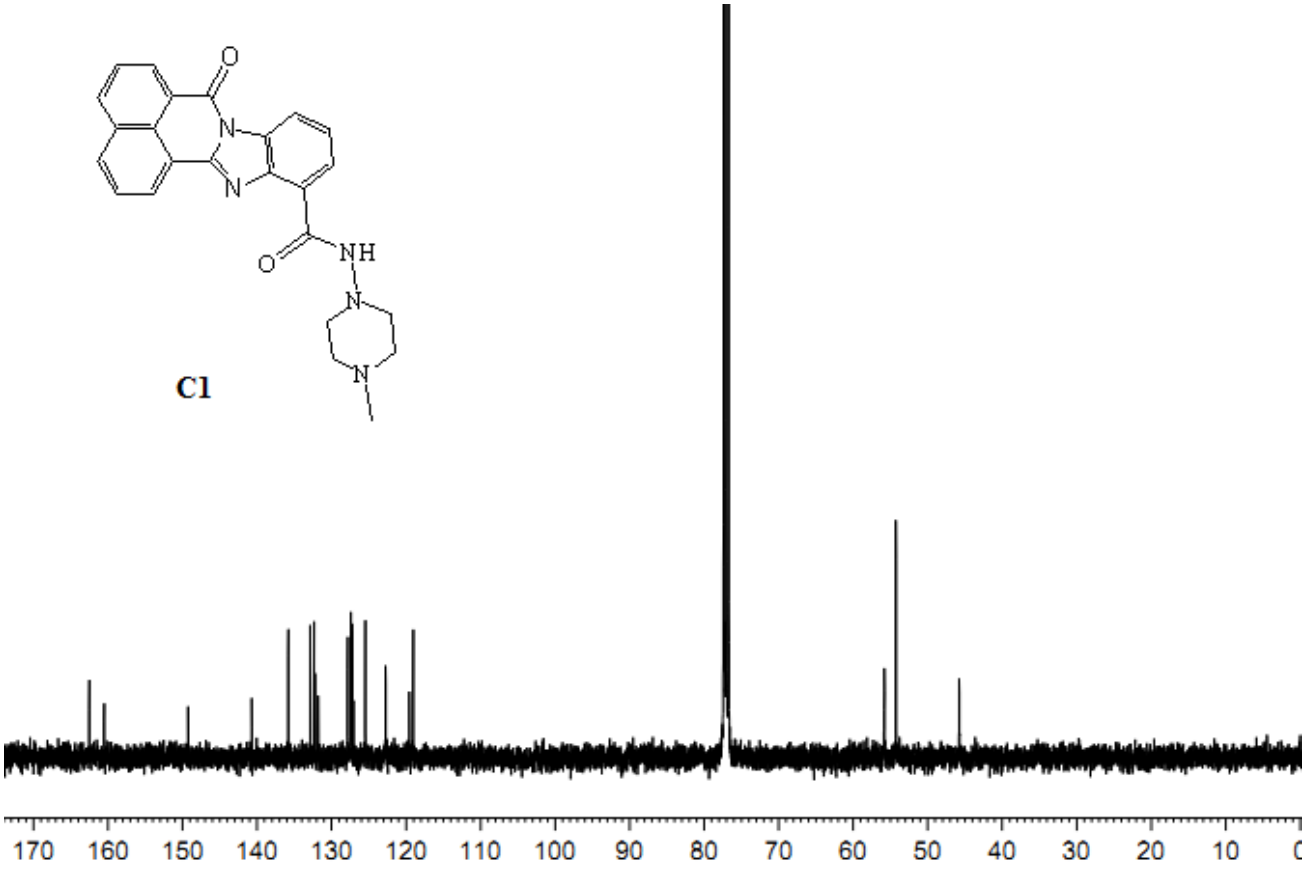


Figure S13. ^{13}C NMR spectra of **C1** in $CDCl_3$.

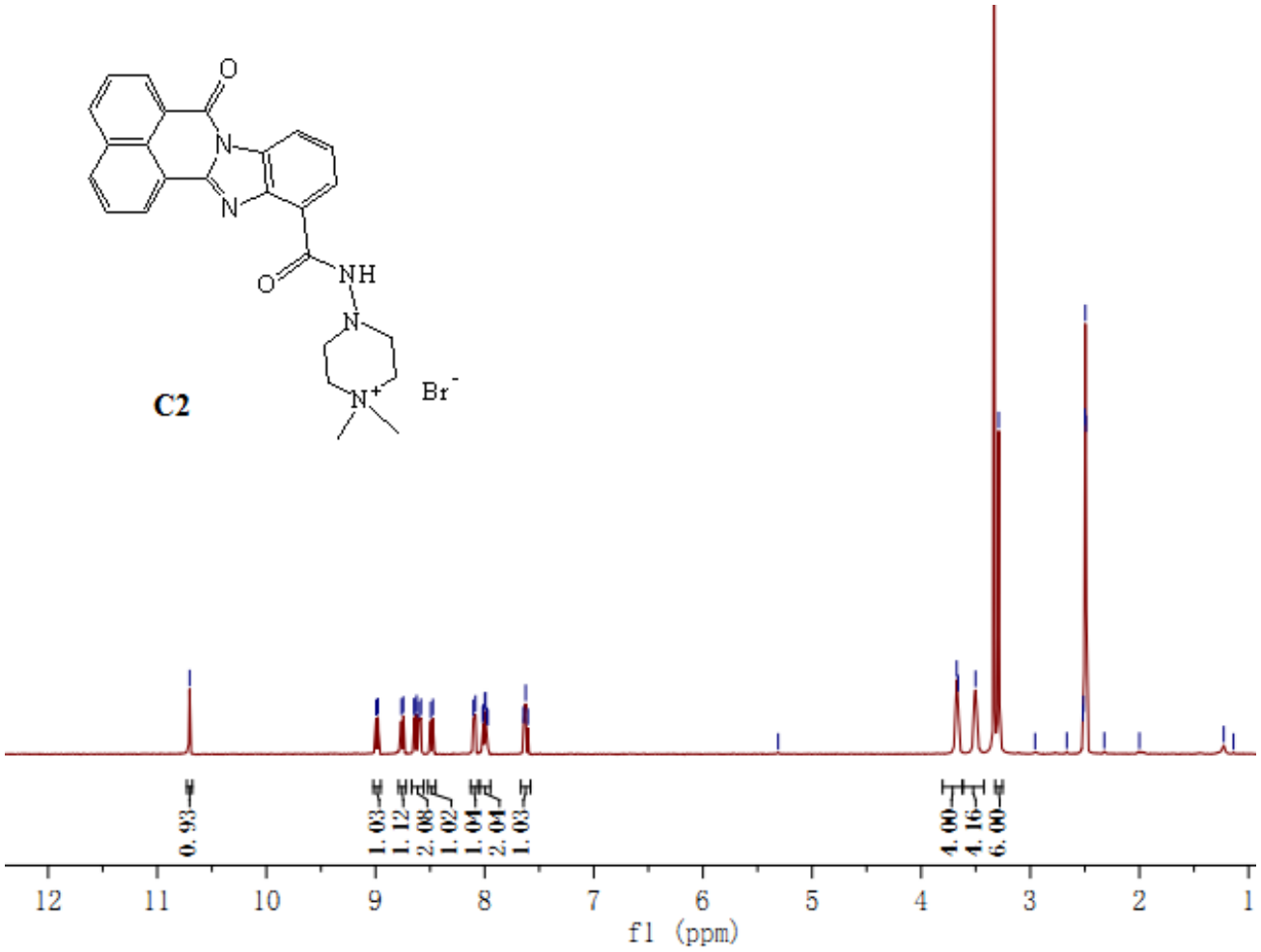


Figure S14. ^{1}H NMR spectra of **C2** in DMSO.

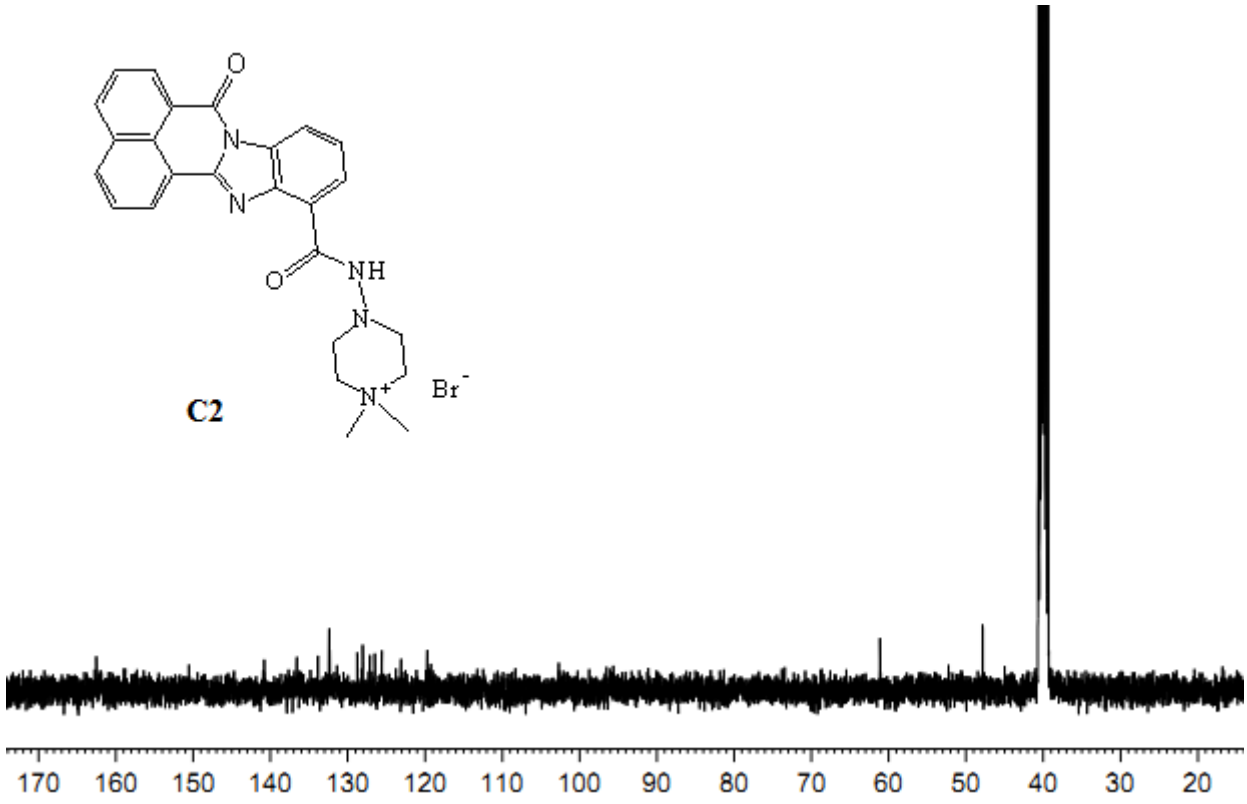


Figure S15. ^{13}C NMR spectra of **C2** in DMSO.

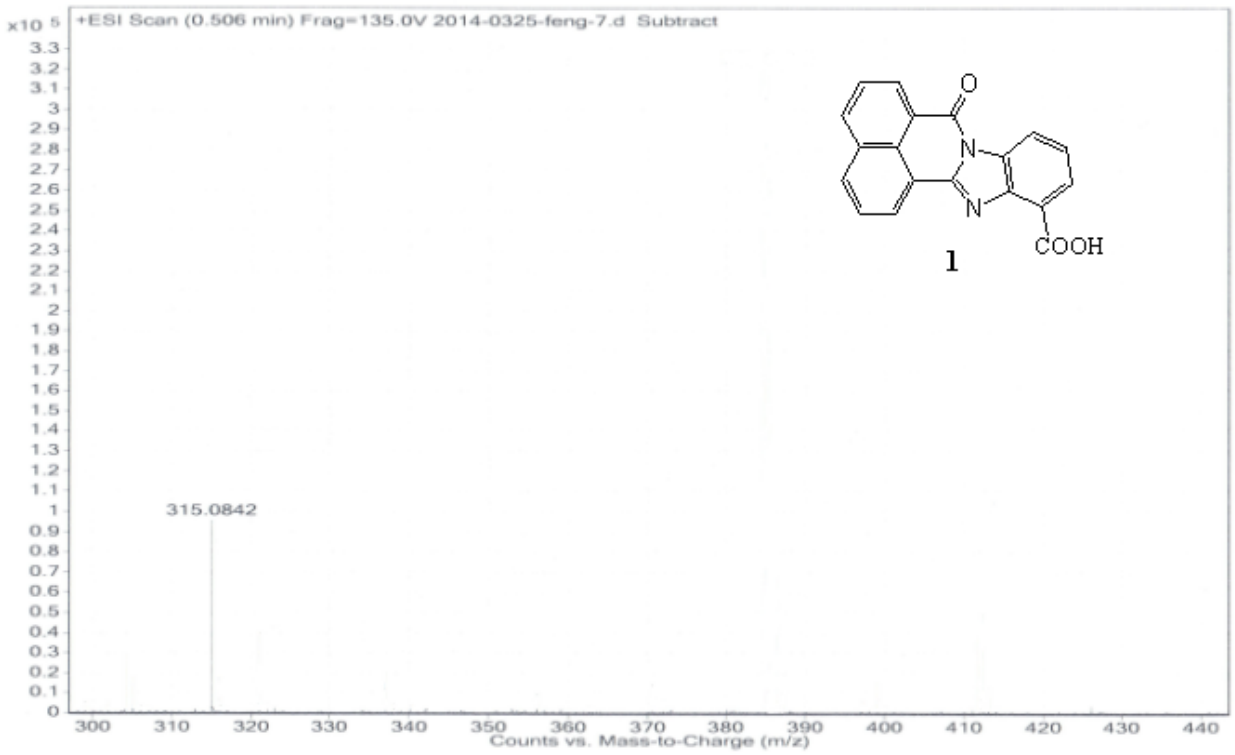


Figure S16. The mass spectrum of compound **1** (benzimidazo[2,1-a]benz[de]isoquinoline-7-one-10-carboxylic acid).

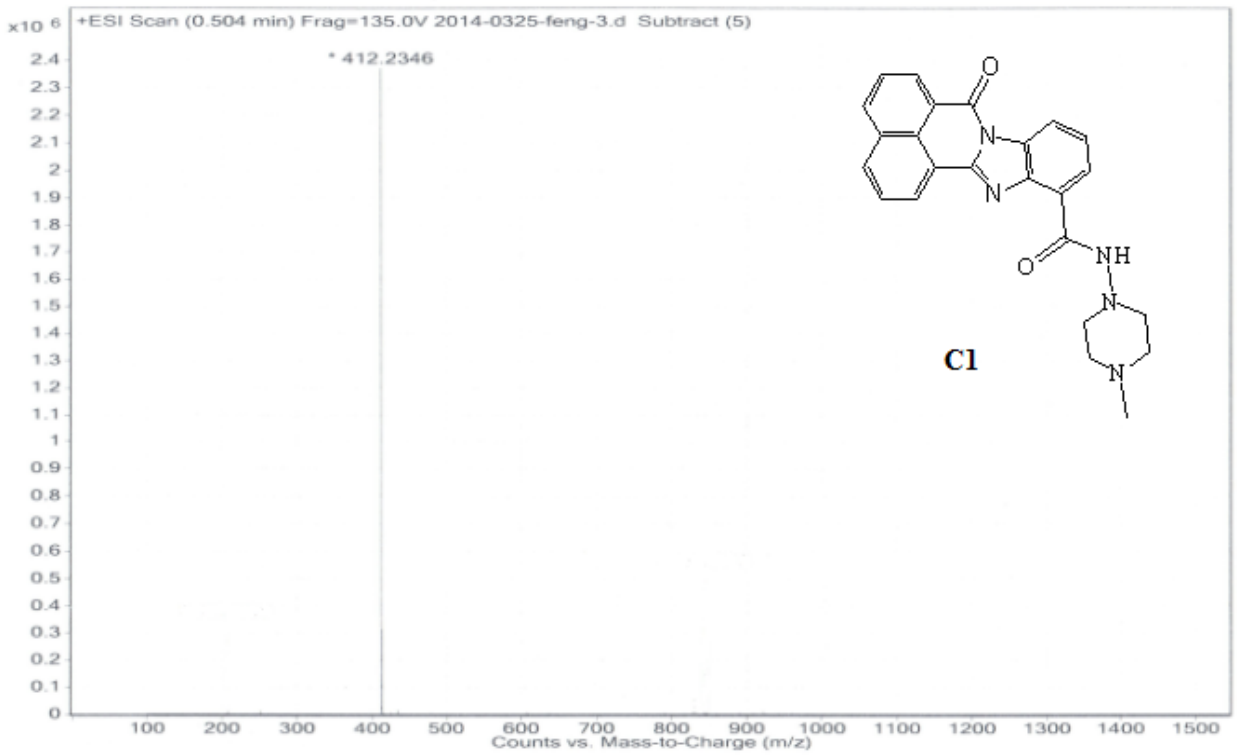


Figure S17. The mass spectrum of **C1**.

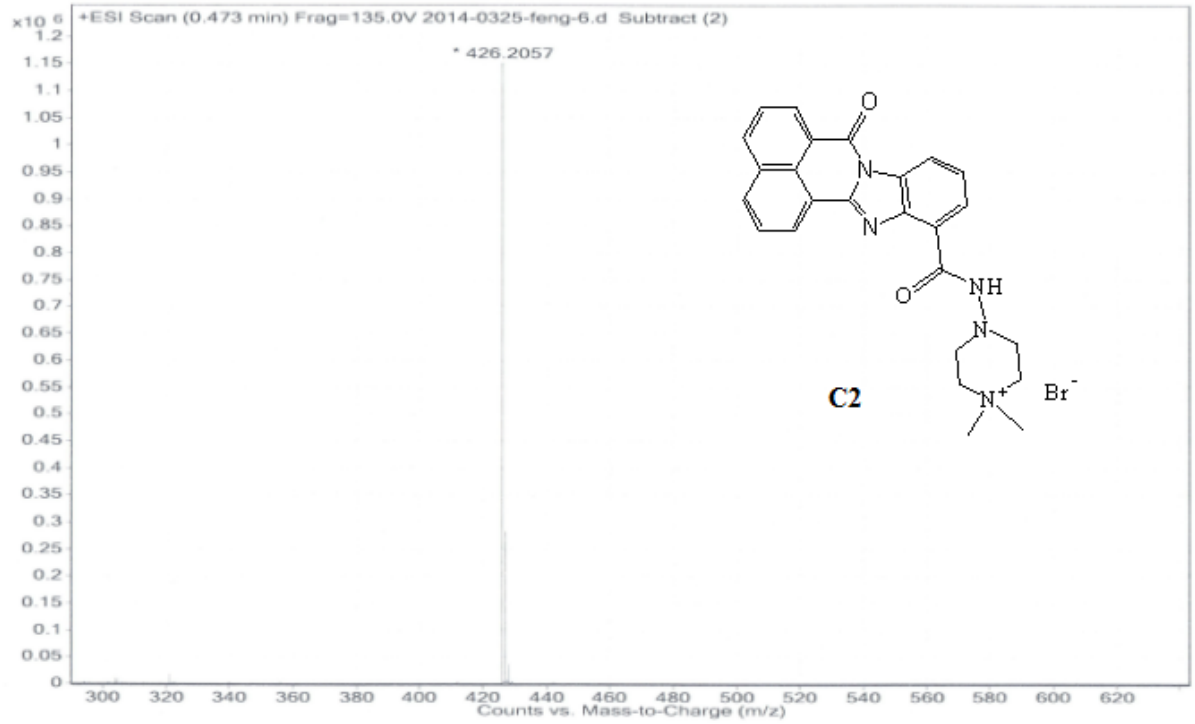


Figure S18. The mass spectrum of **C2**.

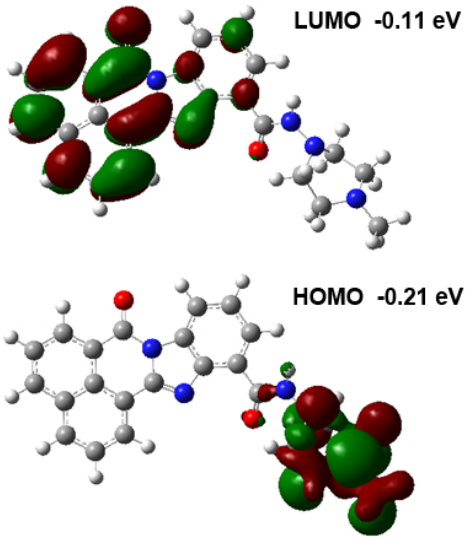


Figure S19. Frontier molecular orbitals (MO) of sensor **C1** calculated with Time-dependent density functional theory (TDDFT) at the B3LYP/6-31+G(d) level using Gaussian 03.

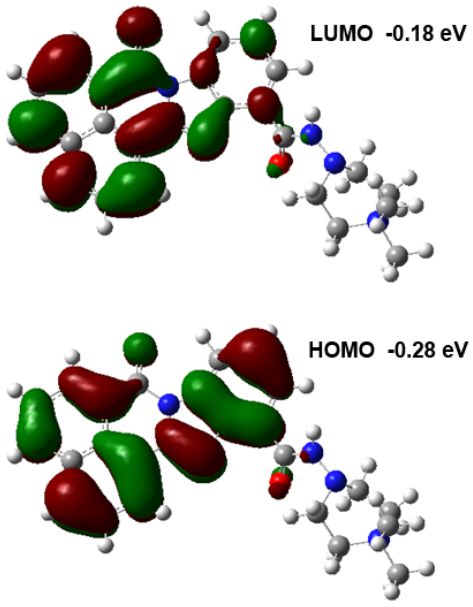
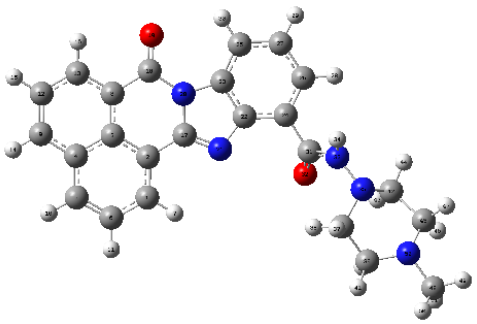


Figure S20. Frontier molecular orbitals (MO) of neutral sensor **C2** calculated with Time-dependent density functional theory (TDDFT) at the B3LYP/6-31+G(d) level using Gaussian 03.

Table S2. XYZ coordinate of the optimized structure of **C1**.

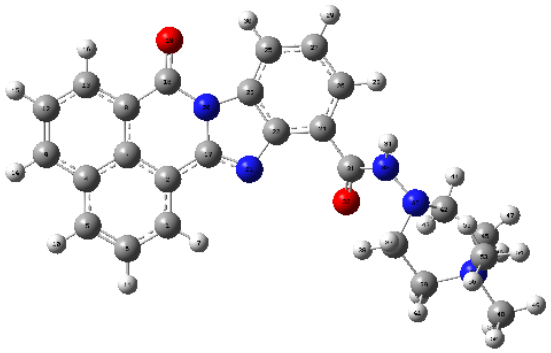


Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	2.282861	-2.565300	0.275230
2	6	0	2.734694	-1.260921	0.131758
3	6	0	4.127543	-0.993159	-0.009708
4	6	0	5.051685	-2.083752	-0.006606
5	6	0	4.552618	-3.406455	0.139340
6	6	0	3.197675	-3.638578	0.277851
7	1	0	1.217764	-2.742526	0.387765
8	6	0	4.619456	0.338296	-0.152330
9	6	0	6.437514	-1.804976	-0.148190
10	1	0	5.255973	-4.235751	0.142252
11	1	0	2.827799	-4.653633	0.391676
12	6	0	6.892194	-0.507699	-0.285560
13	6	0	5.980331	0.568133	-0.287269
14	1	0	7.140854	-2.634589	-0.146085
15	1	0	7.954922	-0.309860	-0.392189
16	1	0	6.327775	1.591155	-0.393045
17	6	0	1.823211	-0.131881	0.123216
18	6	0	3.696464	1.501420	-0.158665
19	8	0	4.050826	2.665232	-0.279543
20	7	0	2.339549	1.170034	-0.012575
21	7	0	0.519997	-0.154339	0.230420
22	6	0	0.119138	1.172814	0.175323
23	6	0	1.233850	2.029734	0.013564
24	6	0	-1.179423	1.709840	0.227729
25	6	0	1.115071	3.414774	-0.096077
26	6	0	-1.303662	3.097833	0.104948
27	6	0	-0.180829	3.931990	-0.047282
28	1	0	-2.292179	3.546848	0.157252

29	1	0	-0.325980	5.006016	-0.122937
30	1	0	1.985173	4.048092	-0.213799
31	6	0	-2.376528	0.825622	0.463498
32	8	0	-2.483236	0.092136	1.439604
33	7	0	-3.351244	0.947803	-0.498464
34	1	0	-3.153977	1.480460	-1.337187
35	7	0	-4.540763	0.211845	-0.527692
36	6	0	-4.323866	-1.239447	-0.729409
37	1	0	-4.202778	-1.409211	-1.806520
38	1	0	-3.419375	-1.581278	-0.211382
39	6	0	-5.534143	-2.029625	-0.208920
40	1	0	-5.425124	-2.234780	0.874743
41	1	0	-5.561114	-3.002739	-0.711738
42	6	0	-5.465664	0.522324	0.567736
43	1	0	-5.107862	0.127162	1.528981
44	1	0	-5.524158	1.610789	0.661175
45	6	0	-6.856809	-0.042714	0.225752
46	1	0	-7.408984	-0.172037	1.177211
47	1	0	-7.422540	0.669994	-0.388550
48	6	0	-7.966249	-2.113965	-0.366092
49	1	0	-8.839421	-1.527723	-0.676075
50	1	0	-7.906168	-2.997634	-1.011293
51	1	0	-8.138196	-2.454152	0.676372
52	7	0	-6.765527	-1.310970	-0.512566

Table S3. XYZ coordinate of the optimized structure of **C2**.

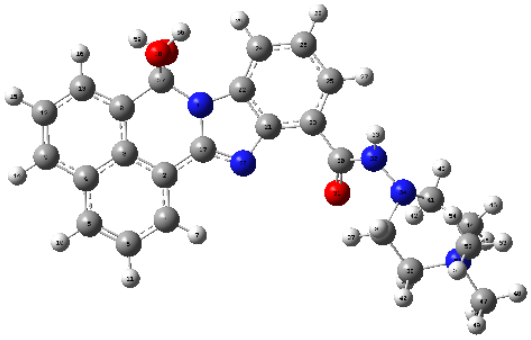


Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-2.682942	-2.607442	-0.186727
2	6	0	-3.103780	-1.285810	-0.085109
3	6	0	-4.494342	-0.976364	0.023269
4	6	0	-5.446778	-2.044788	0.029616
5	6	0	-4.978283	-3.384589	-0.072384
6	6	0	-3.625232	-3.657214	-0.178839
7	1	0	-1.622378	-2.812857	-0.275578
8	6	0	-4.957734	0.371802	0.122308
9	6	0	-6.830285	-1.729661	0.135802
10	1	0	-5.702348	-4.193355	-0.067569
11	1	0	-3.282071	-4.682525	-0.259354
12	6	0	-7.256935	-0.416498	0.230524
13	6	0	-6.318936	0.637135	0.223420
14	1	0	-7.551532	-2.541149	0.140246
15	1	0	-8.314127	-0.190645	0.309827
16	1	0	-6.642599	1.669346	0.295518
17	6	0	-2.167364	-0.186036	-0.089470
18	6	0	-4.012824	1.503217	0.118407
19	8	0	-4.337948	2.702629	0.206002
20	7	0	-2.654104	1.137731	0.006009
21	7	0	-0.844794	-0.229523	-0.175595
22	6	0	-0.420663	1.104477	-0.150267
23	6	0	-1.532122	1.981086	-0.023654
24	6	0	0.883482	1.632231	-0.193922
25	6	0	-1.398710	3.366522	0.058645
26	6	0	1.019107	3.029105	-0.101099
27	6	0	-0.096149	3.876064	0.017389

28	1	0	2.007225	3.473282	-0.169038
29	1	0	0.055422	4.948348	0.066555
30	1	0	-2.265686	4.005685	0.148150
31	6	0	2.064468	0.755537	-0.368371
32	8	0	2.126635	-0.231798	-1.135112
33	7	0	3.180389	1.107809	0.390315
34	1	0	3.136688	1.814671	1.109584
35	7	0	4.382535	0.378145	0.303450
36	6	0	4.248433	-1.023232	0.798773
37	1	0	4.247937	-1.002428	1.892548
38	1	0	3.311152	-1.474942	0.454242
39	6	0	5.399668	-1.875148	0.256655
40	1	0	5.196687	-2.222310	-0.759004
41	1	0	5.584634	-2.744671	0.891768
42	6	0	5.055053	0.472175	-1.011274
43	1	0	4.559143	-0.143014	-1.772256
44	1	0	5.002225	1.511028	-1.344082
45	6	0	6.531587	0.091792	-0.838125
46	1	0	6.960902	-0.234151	-1.788012
47	1	0	7.121648	0.921164	-0.444839
48	6	0	7.826821	-1.994117	-0.298386
49	1	0	8.732309	-1.402362	-0.439953
50	1	0	7.999240	-2.762497	0.456593
51	1	0	7.531493	-2.456196	-1.241146
52	7	0	6.712249	-1.078103	0.174960
53	6	0	7.077362	-0.520399	1.545299
54	1	0	8.064655	-0.061244	1.476956
55	1	0	6.331191	0.223419	1.818370
56	1	0	7.097370	-1.340740	2.264493

Table S4. XYZ coordinate of the optimized structure of **C2**+OH^-.



Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	2.353324	2.708566	-0.297819
2	6	0	2.842318	1.419042	-0.137740
3	6	0	4.247832	1.184975	-0.004473
4	6	0	5.141952	2.307034	-0.027626
5	6	0	4.602917	3.614684	-0.199524
6	6	0	3.239420	3.809377	-0.331677
7	1	0	1.284104	2.853782	-0.403046
8	6	0	4.778709	-0.124741	0.174418
9	6	0	6.537171	2.082288	0.134591
10	1	0	5.283899	4.460354	-0.221937
11	1	0	2.842371	4.810386	-0.462688
12	6	0	7.026313	0.804839	0.331894
13	6	0	6.141647	-0.299341	0.361097
14	1	0	7.211827	2.932943	0.113160
15	1	0	8.088696	0.640067	0.475153
16	1	0	6.539927	-1.288406	0.566174
17	6	0	1.961375	0.272933	-0.115440
18	8	0	4.094423	-1.976805	1.479771
19	7	0	2.485989	-1.017991	-0.015591
20	7	0	0.632754	0.272445	-0.220005
21	6	0	0.257929	-1.068836	-0.209465
22	6	0	1.405678	-1.903090	-0.086012
23	6	0	-1.025249	-1.645827	-0.277738
24	6	0	1.314953	-3.297220	-0.066631
25	6	0	-1.115728	-3.046443	-0.216321
26	6	0	0.033691	-3.855703	-0.126324
27	1	0	-2.087354	-3.524506	-0.297152

28	1	0	-0.076458	-4.934669	-0.126582
29	1	0	2.194855	-3.928733	-0.053064
30	6	0	-2.234406	-0.803633	-0.446737
31	8	0	-2.360446	0.118131	-1.284996
32	7	0	-3.294426	-1.112757	0.401429
33	1	0	-3.195390	-1.773258	1.160043
34	7	0	-4.509324	-0.397985	0.349364
35	6	0	-4.360626	1.029810	0.758537
36	1	0	-4.336408	1.073824	1.852148
37	1	0	-3.427614	1.457266	0.371907
38	6	0	-5.516035	1.855365	0.189337
39	1	0	-5.346879	2.108598	-0.859714
40	1	0	-5.656523	2.781257	0.752597
41	6	0	-5.270302	-0.582855	-0.906482
42	1	0	-4.828974	-0.025639	-1.742726
43	1	0	-5.239734	-1.643609	-1.166216
44	6	0	-6.730652	-0.186634	-0.661182
45	1	0	-7.233763	0.034671	-1.605316
46	1	0	-7.279376	-0.972011	-0.138420
47	6	0	-7.957508	1.976898	-0.291302
48	1	0	-8.882793	1.399960	-0.330566
49	1	0	-8.077508	2.827126	0.381968
50	1	0	-7.692248	2.325900	-1.290150
51	7	0	-6.846245	1.084705	0.232784
52	6	0	-7.172689	0.681509	1.664806
53	1	0	-8.165732	0.229610	1.676375
54	1	0	-6.428025	-0.038448	1.999799
55	1	0	-7.163349	1.574583	2.292106
56	1	0	3.639278	-2.844972	1.516712
57	6	0	3.882543	-1.348665	0.194672
58	8	0	4.178501	-2.315541	-0.844995
59	1	0	5.144656	-2.447281	-0.935834
