Electronic Supplementary Material (ESI) for New Journal of Chemistry.

A coumarin based fluorescent chemodosimeter for phosgene gas detection instantaneously in solution and gas phase

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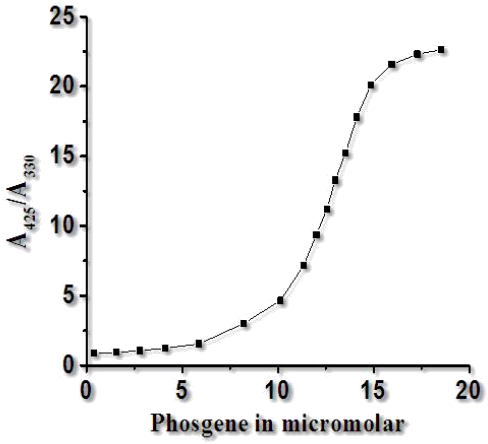


Fig. S1: Change of absorption ratio (A_{425}/A_{330}) of DCCO in the presence of 1 eqv. of triphosgene/triethylamine.

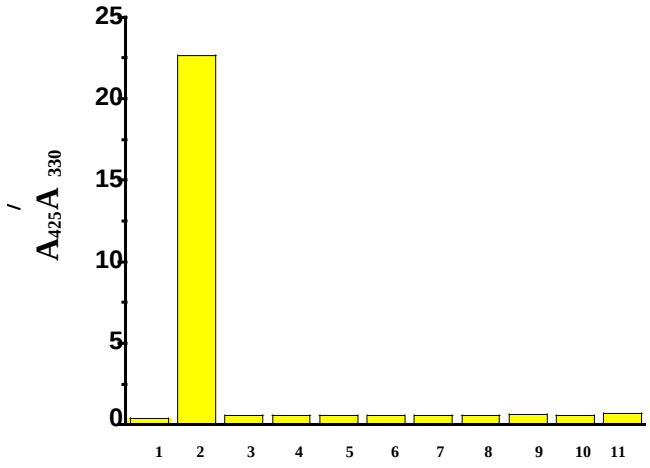


Fig. S2 Bars represent the ratio of absorption (A_{425}/A_{330}): (1) DCCO (2) phosgene (triphosgene/TEA) and other analytes (3) DCNP (4) DCP (5) Triphogene (6) TFA (7) p-TsCl (8) $SOCl_2$ (9) $POCl_3$ (10) $(COCl)_2$ (11) CH_3COCl.

Calculation of the detection limit:

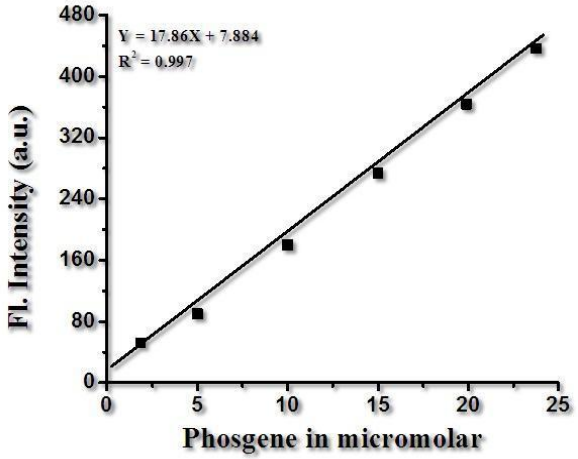


Fig. S3. Fluorescence change at 488 nm of DCCO upon gradual addition of Phosgene.

The detection limit DL of **DCCO** for Phosgene was determined from the following equation [1]:
DL = K* Sb1/S

Where K = 2 or 3 (we take 2 in this case); Sb1 is the standard deviation of the blank solution; S is the slope of the calibration curve. From the graph, we get slope = 17.86, and Sb1 value is 1.0716. Thus using the formula we get the Detection Limit = 0.12 µM i.e. DCCO can detect hydrazine in this minimum concentration.

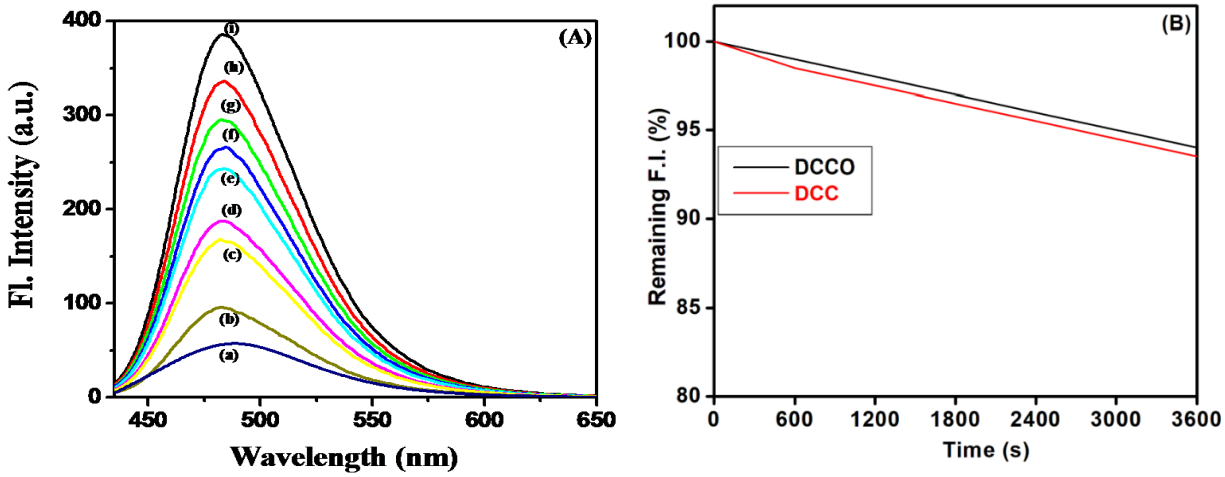


Fig. S4 (A) Time vs fluorescence spectra of DCCO (10 µM) in CH_3CN−TEA at 25 °C upon addition of triphosgene (50 µM) at different times [(b) 5, (c) 10, (d) 15, (e) 20, (f) 30, (g) 40 (h) 50 and (i) 60s] (λ_{ex} = 425 nm). (B) The remaining relative fluorescence intensities of DCCO

(black) and Probe-Phosgene (DCC) (red) as a function of irradiation time (0 − 3600 s). Fluorescence intensities were measured at 480 nm for DCCO and at 487 nm for DCC. Irradiated at 485 nm.

Calculation of Rate Constant:

From the time vs. absorbance at fixed wavelength (487 nm) plot using first order rate equation (Figure S5), we get rate constant (K) = Slope × 2.303 = 0.0699 × 2.303 = 16 × 10^{-2} s^{-1}.

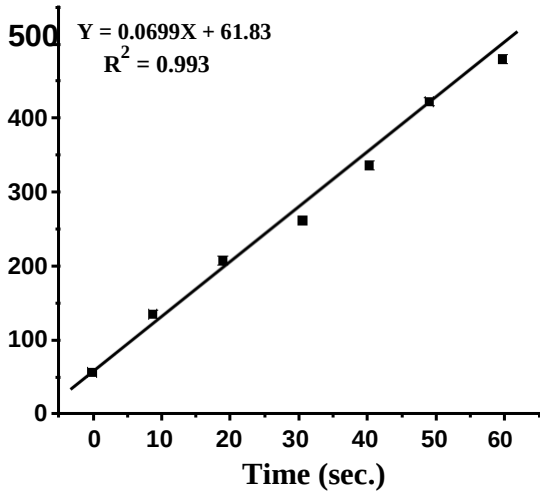


Fig. S5. The time vs. fluorescence at a fixed wavelength (464 nm) plot using first order rate equation.

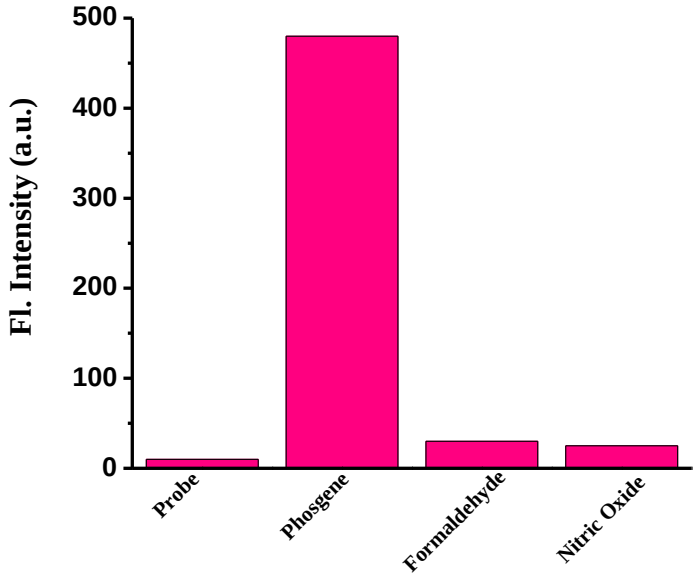


Fig. S6. Fluorescent increment of probe (DCCO) in the presence of formaldehyde and nitric oxide.

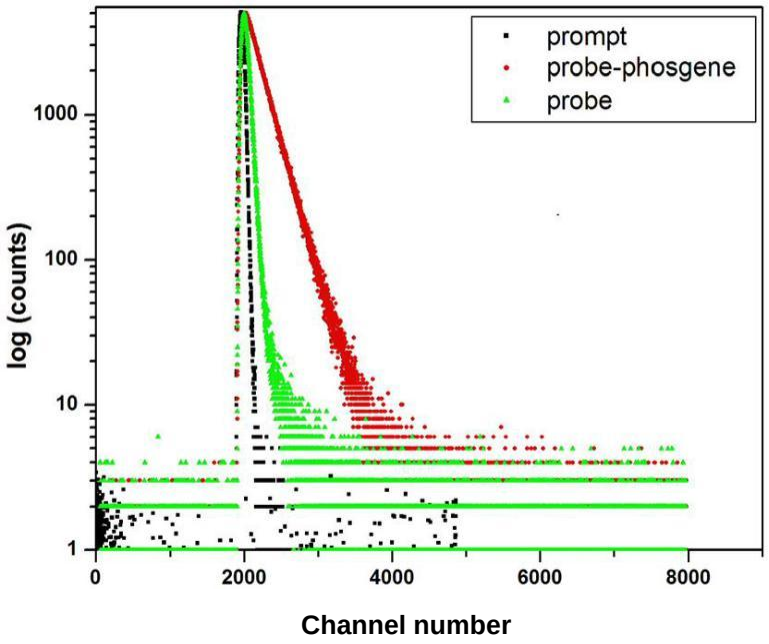


Fig. S7. Time resolved fluorescence decay curve for probe and the probe in the presence of phosgene in CH_3CN.

Table S1. Quantum yield and fluorescence life time data of DCCO and DCC

Species	ϕ	ϒ	k_r ($10^6 \times s^{-1}$)	k_{nr} ($10^8 \times s^{-1}$)
DCCO	0.004	0.667	5.99	14.8
DCC	0.52	3.22	161.4	1.48

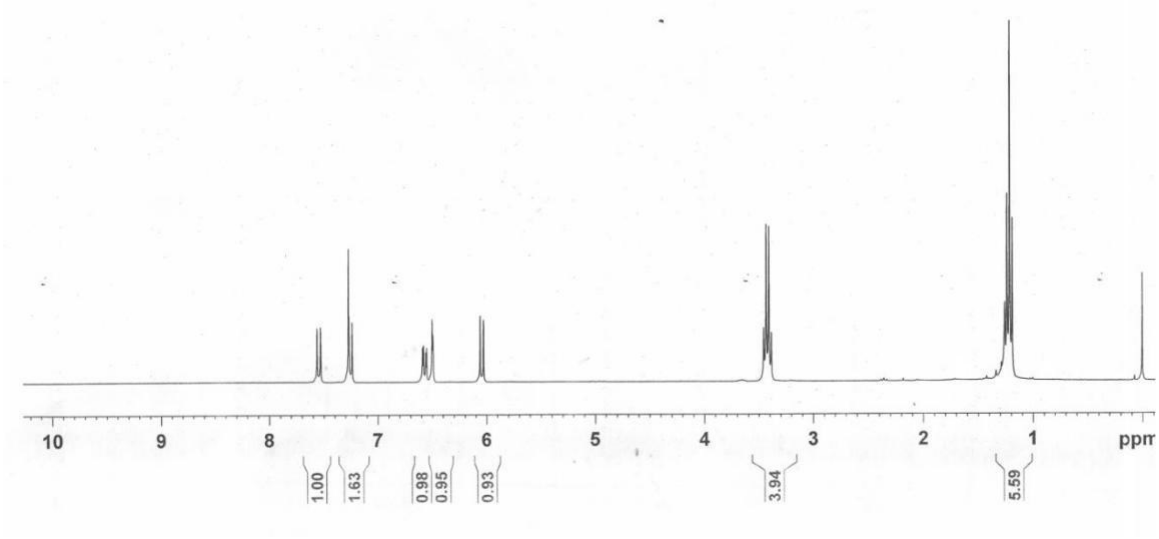


Fig. S8. ^{1}H NMR of coumarin in $CDCl_3$.

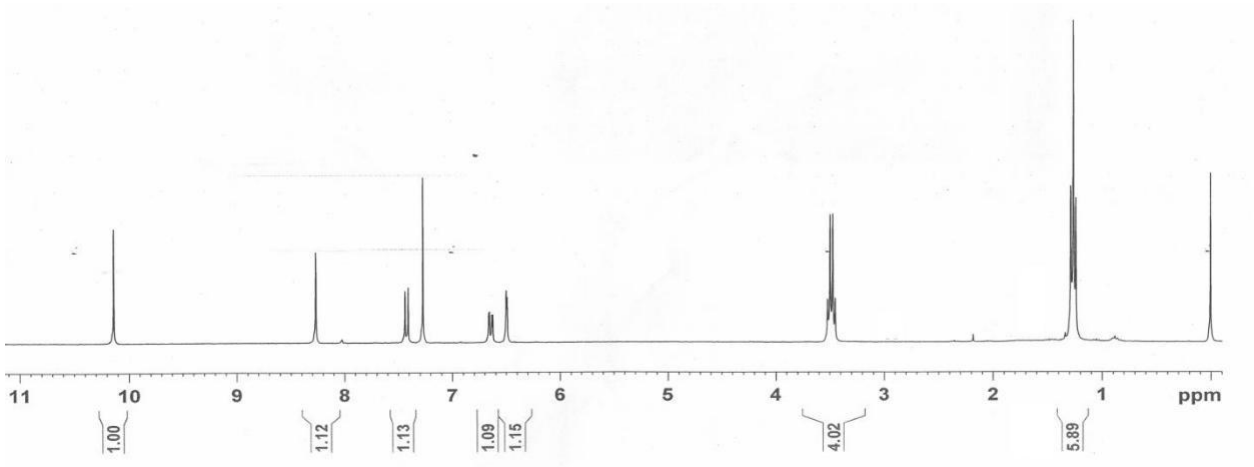


Fig. S9. ^{1}HNMR of 7-diethylamino coumarin-3-aldehyde (**3**) in $CDCl_3$.

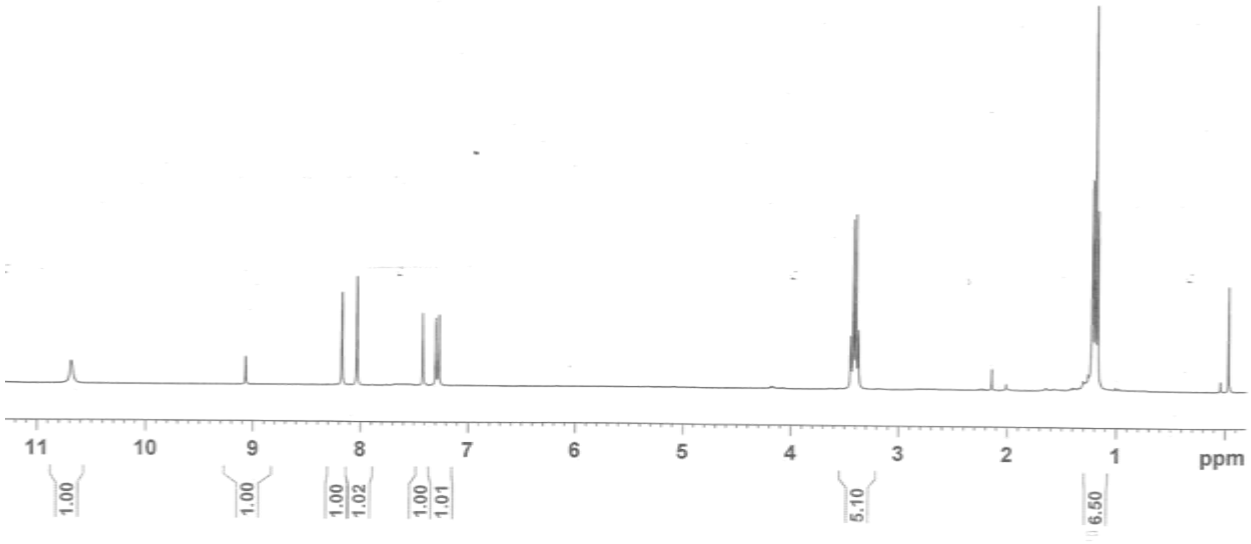


Fig. S10. ^{1}H NMR of DCCO in $CDCl_3$.

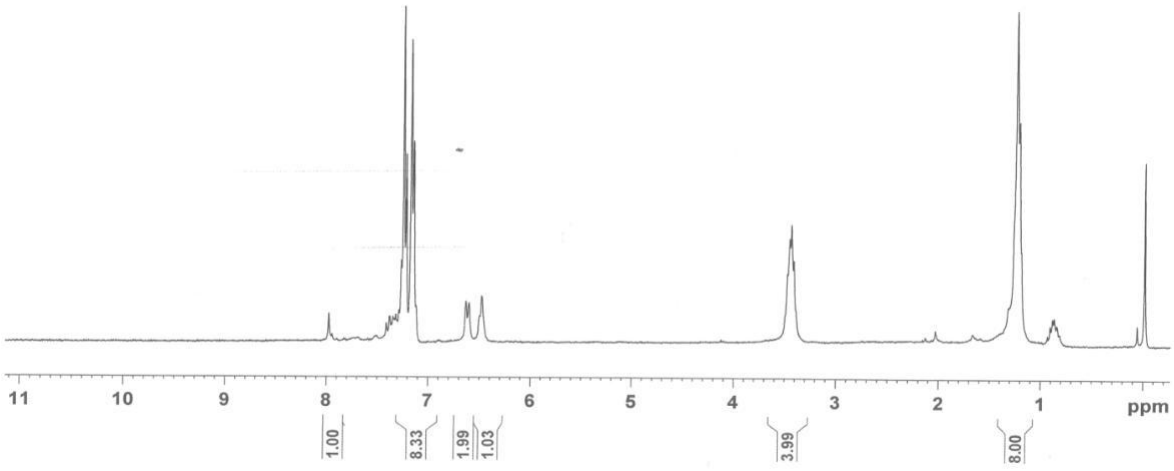


Fig. S11. ^{1}H NMR of DCC in $CDCl_3$.

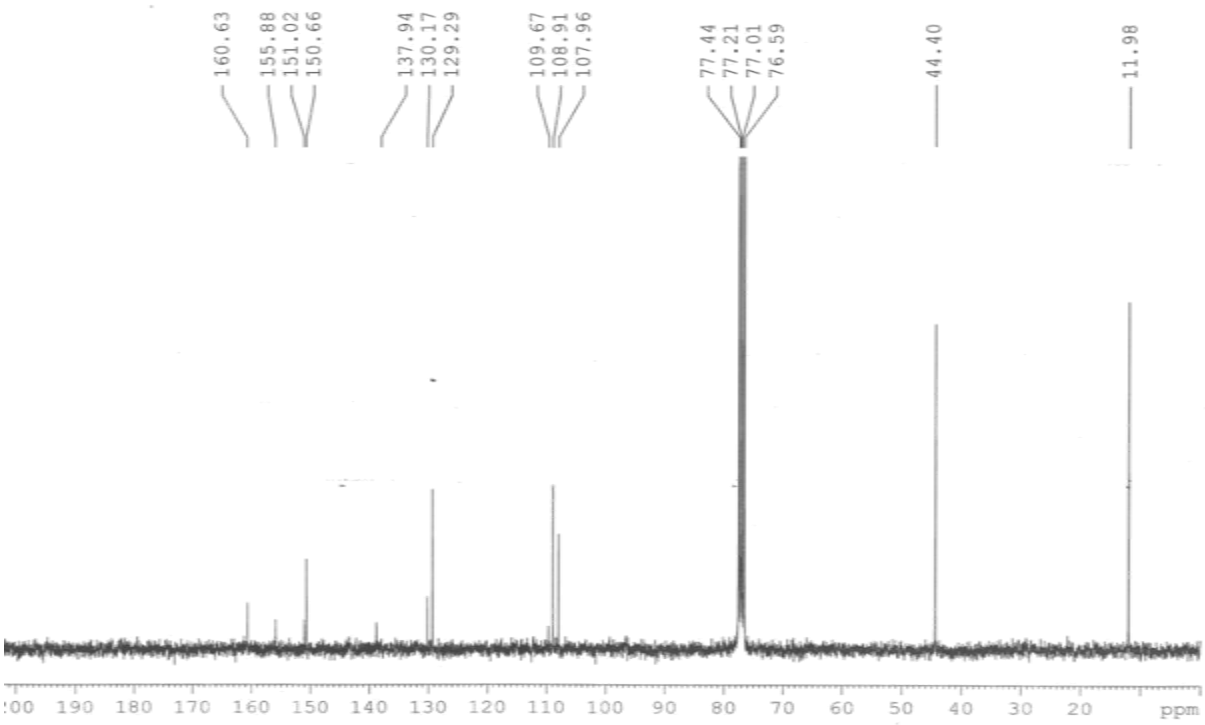


Fig. S12. ^{13}C NMR of DCCO in $CDCl_3$.

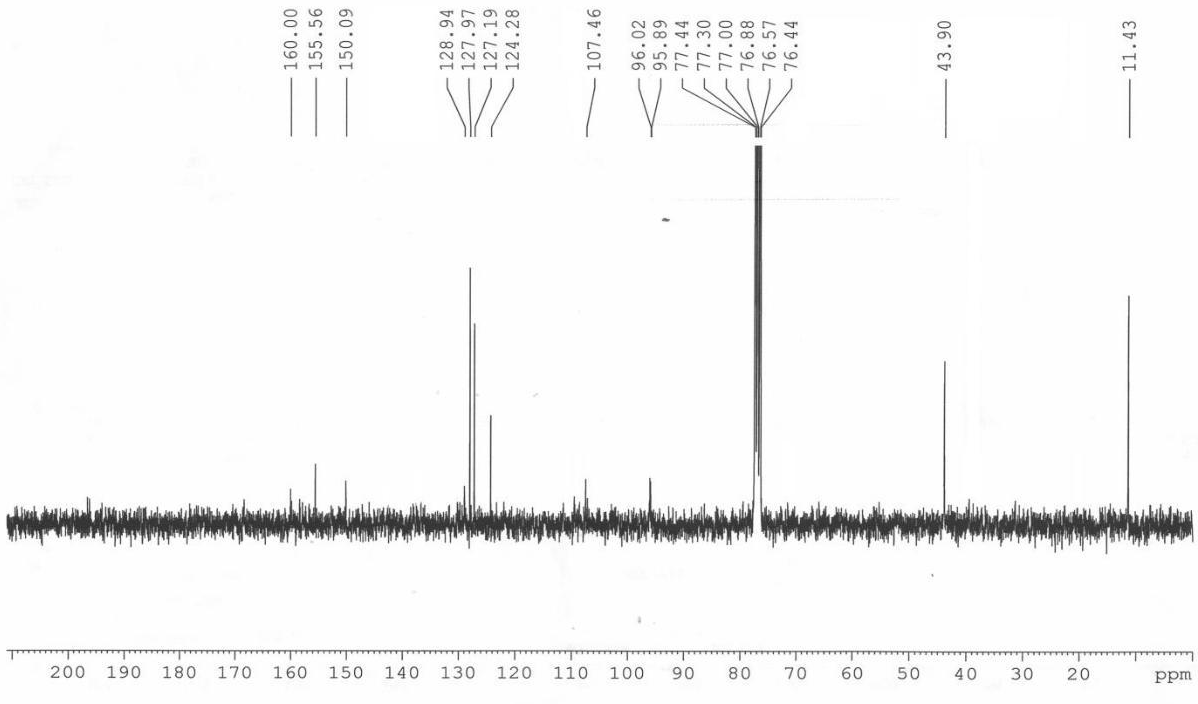


Fig. S13. ^{13}C NMR of DCCO in $CDCl_3$.

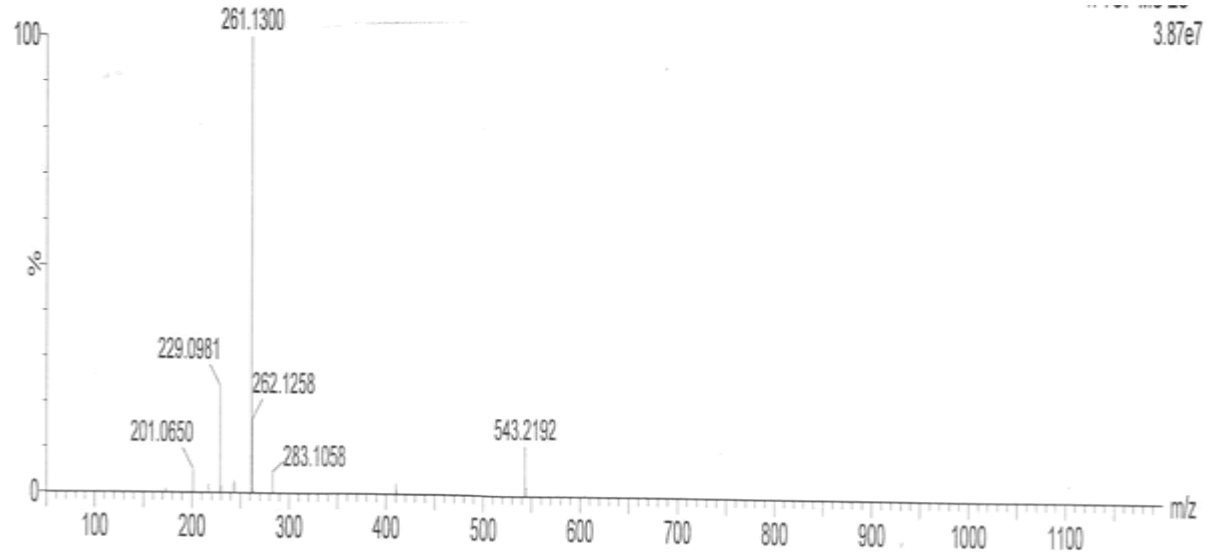


Fig. S14. ESI TOP Mass spectrum of DCCO.

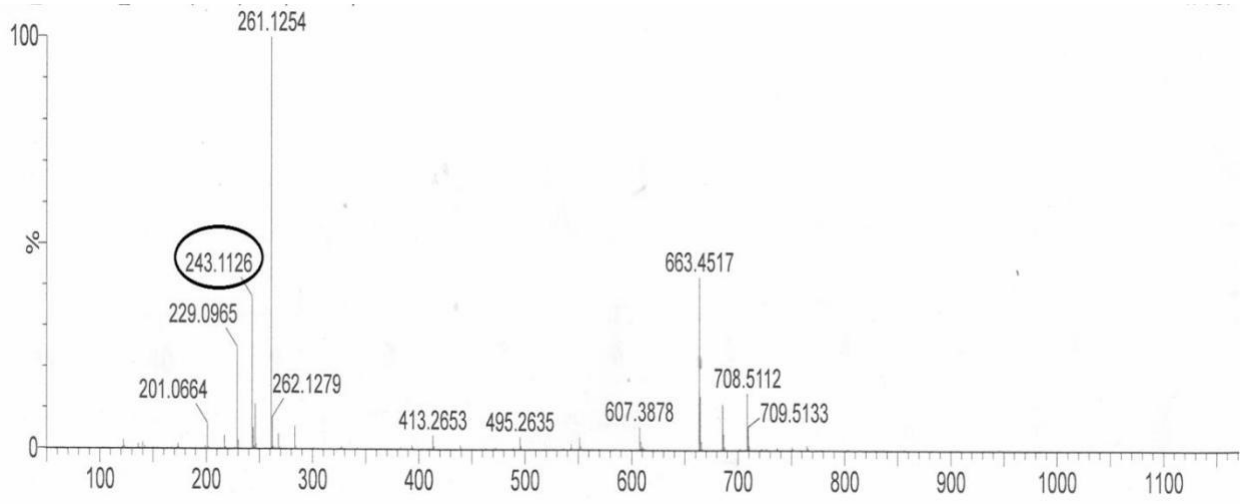


Fig. S15. ESI TOP Mass spectrum of DCC.

Data related to DFT-D3 analysis

Table S2. Geometry optimized Coordinates of DCCO

35

total energy: -877.19447198006 Hartree

O	3.1748928	4.1413507	2.9705822
O	1.8704742	5.8974182	2.6703089
N	0.6314182	7.0353012	4.9825525
C	3.7895560	3.1877613	3.7241845
C	4.5964564	2.2716162	3.0670547
C	5.2608186	1.2509807	3.7981498
C	5.0742195	1.2303970	5.2206765
C	4.2656817	2.1530482	5.8494383
C	3.5925632	3.1652409	5.1238165
C	2.7468472	4.1511912	5.6908977
C	2.1230183	5.1133860	4.9244048
C	2.3385837	5.1258495	3.4759668
C	1.2658800	6.0921278	5.5799603
H	4.6956532	2.3696013	1.9890079
H	5.5738047	0.4788733	5.8274863
H	4.1389969	2.1103574	6.9341857
H	2.5856783	4.1440700	6.7730477
H	1.1726209	5.9926787	6.6730726
N	6.0344813	0.3156154	3.1706673
C	6.7700390	-0.6964743	3.9302015
C	8.0797767	-0.1985752	4.5450382
H	6.1143699	-1.1084997	4.7126395
H	8.5568874	-1.0082093	5.1200822
H	7.9071691	0.6485212	5.2269012
H	8.7853735	0.1291212	3.7667966
H	6.9763491	-1.5275665	3.2408699
C	6.2638475	0.3745911	1.7270644

C	7.3327224	1.3810904	1.2952276
H	5.3101018	0.5918860	1.2210872
H	7.4212473	1.3865324	0.1971658
H	8.3161569	1.1217533	1.7157843
H	7.0810173	2.4021194	1.6216718
H	6.5543495	-0.6355189	1.4048161
O	-0.0939040	7.7927709	5.8925096
H	-0.5240578	8.4642504	5.3423961

Table S3. Geometry optimized Coordinates of the phosgene reacted product (DCC)

total energy: -800.90146273666Hartree

32

O	4.1089428	4.1825837	5.9210247
O	3.3917040	5.9725768	7.0151175
C	3.9367504	3.1154154	5.0876434
C	5.0402354	2.3217077	4.8367863
C	4.9288973	1.1914175	3.9795754
C	3.6443821	0.9309895	3.3892866
C	2.5615362	1.7359100	3.6543594
C	2.6649786	2.8596611	4.5135673
C	1.6011619	3.7312703	4.8271604
C	1.7985815	4.8056899	5.6753006
C	3.1095623	5.0654024	6.2645173
N	5.9940316	0.3803976	3.7383154

C 7.3141758 0.6807326 4.2981878

C 8.0966134 1.7452319 3.5269577

C 5.8976341 -0.7507980 2.8113894

C 6.0115223 -0.3656333 1.3356211

H 5.9778048 2.5969935 5.3125032

H 3.5118072 0.0860688 2.7179544

H 1.5956426 1.5143055 3.1942617

H 0.6137640 3.5520444 4.3948974

H 7.1967381 0.9796798 5.3509531

H 9.0596372 1.9361327 4.0265499

H 7.5437563 2.6959883 3.4777356

H 8.3055174 1.4180815 2.4972139

H 7.8791606 -0.2615743 4.3106716

H 4.9553420 -1.2883504 2.9959228

H 5.9055679 -1.2632879 0.7061419

H 6.9886894 0.0909608 1.1172250

H 5.2274633 0.3503532 1.0445373

H 6.7022322 -1.4502867 3.0771749

C 0.7476061 5.7037134 6.0158690 N -

0.1149812 6.4339863 6.2912600

Table S4. Vibrational stretching of DCCO.

mode	symmetry	wave number	IR intensity	selection rules	
		cm**(-1)	km/mol	IR	Raman
1		0.00	0.00000	-	-
2		0.00	0.00000	-	-
3		0.00	0.00000	-	-
4		0.00	0.00000	-	-
5		0.00	0.00000	-	-
6		0.00	0.00000	-	-
7	a	18.87	1.01377	YES	YES
8	a	26.96	2.04960	YES	YES
9	a	67.55	0.85044	YES	YES
10	a	77.84	0.11687	YES	YES
11	a	102.68	1.97729	YES	YES
12	a	114.04	0.35135	YES	YES
13	a	126.41	1.76818	YES	YES
14	a	129.55	3.03741	YES	YES
15	a	166.22	0.72514	YES	YES
16	a	179.51	0.22588	YES	YES
17	a	213.37	0.16866	YES	YES
18	a	226.83	0.33317	YES	YES
19	a	248.40	0.29881	YES	YES
20	a	270.89	0.07457	YES	YES

21	a	282.72	1.84367	YES	YES
22	a	295.58	0.23247	YES	YES
23	a	366.86	13.51446	YES	YES
24	a	374.69	7.40230	YES	YES
25	a	384.19	178.96302	YES	YES
26	a	407.38	9.98057	YES	YES
27	a	422.08	11.47532	YES	YES
28	a	451.55	4.67304	YES	YES
29	a	462.46	23.35591	YES	YES
30	a	479.27	41.10123	YES	YES
31	a	494.60	18.29064	YES	YES
32	a	510.80	6.99578	YES	YES
33	a	551.29	43.89789	YES	YES
34	a	583.63	5.97774	YES	YES
35	a	633.48	8.28341	YES	YES
36	a	668.52	5.19055	YES	YES
37	a	707.18	107.44856	YES	YES
38	a	745.89	1.46418	YES	YES
39	a	759.61	77.62793	YES	YES
40	a	784.04	12.36441	YES	YES
41	a	786.24	32.57727	YES	YES
42	a	787.97	8.34704	YES	YES
43	a	809.52	64.40223	YES	YES

44	a	822.66	26.98821	YES	YES
45	a	863.37	61.31618	YES	YES
46	a	887.23	33.34150	YES	YES
47	a	904.23	7.63721	YES	YES
48	a	932.83	4.36130	YES	YES
49	a	945.95	2.56435	YES	YES
50	a	979.64	14.36883	YES	YES
51	a	985.79	6.05649	YES	YES
52	a	994.04	11.84476	YES	YES
53	a	1001.73	693.10422	YES	YES
54	a	1035.07	44.78051	YES	YES
55	a	1074.30	2.27852	YES	YES
56	a	1081.82	0.03694	YES	YES
57	a	1096.48	111.67595	YES	YES
58	a	1104.87	29.67984	YES	YES
59	a	1152.44	217.31201	YES	YES
60	a	1167.65	0.85949	YES	YES
61	a	1207.75	317.60452	YES	YES
62	a	1214.16	35.02577	YES	YES
63	a	1240.44	155.52678	YES	YES
64	a	1284.03	12.86151	YES	YES
65	a	1291.43	31.07746	YES	YES
66	a	1304.05	191.25073	YES	YES

67	a	1320.50	35.45138	YES	YES
68	a	1331.04	36.60633	YES	YES
69	a	1363.09	20.37139	YES	YES
70	a	1374.66	358.16215	YES	YES
71	a	1385.96	23.66077	YES	YES
72	a	1390.11	160.32875	YES	YES
73	a	1395.73	37.69384	YES	YES
74	a	1400.14	7.75711	YES	YES
75	a	1436.26	63.77606	YES	YES
76	a	1443.84	10.89365	YES	YES
77	a	1445.48	368.04236	YES	YES
78	a	1451.72	1.28908	YES	YES
79	a	1452.72	1.22720	YES	YES
80	a	1461.66	259.19617	YES	YES
81	a	1470.80	6.78955	YES	YES
82	a	1489.33	14.38804	YES	YES
83	a	1508.68	127.82967	YES	YES
84	a	1551.72	919.86411	YES	YES
85	a	1579.35	23.32902	YES	YES
86	a	1638.79	1386.57223	YES	YES
87	a	1665.29	1225.62792	YES	YES
88	a	1701.07	56.76342	YES	YES
89	a	1803.59	917.09439	YES	YES

90	a	3033.63	9.80385	YES	YES
91	a	3035.88	38.37512	YES	YES
92	a	3054.05	37.58975	YES	YES
93	a	3059.29	110.63552	YES	YES
94	a	3089.24	34.11195	YES	YES
95	a	3101.10	2.90898	YES	YES
96	a	3107.29	5.22263	YES	YES
97	a	3118.66	44.74438	YES	YES
98	a	3120.40	78.26346	YES	YES
99	a	3125.92	22.08381	YES	YES
100	a	3131.83	59.98035	YES	YES
101	a	3174.77	10.77977	YES	YES
102	a	3185.63	7.70485	YES	YES
103	a	3238.46	6.94292	YES	YES
104	a	3243.00	1.97201	YES	YES
105	a	3787.71	403.28957	YES	YES

Table S5. Vibrational stretching of DCC.

mode	symmetry	wave number	IR intensity	selection rules	
		cm**(-1)	km/mol	IR	Raman
1		-0.00	0.00000	-	-
2		0.00	0.00000	-	-
3		0.00	0.00000	-	-

4		0.00	0.00000	-	-
5		0.00	0.00000	-	-
6		0.00	0.00000	-	-
7	a	30.22	0.99649	YES	YES
8	a	39.69	0.53591	YES	YES
9	a	69.99	1.24522	YES	YES
10	a	98.93	3.68968	YES	YES
11	a	113.53	0.81675	YES	YES
12	a	119.95	3.67145	YES	YES
13	a	132.10	1.56870	YES	YES
14	a	177.30	3.03188	YES	YES
15	a	184.40	1.80527	YES	YES
16	a	224.05	1.19959	YES	YES
17	a	234.10	0.32624	YES	YES
18	a	264.46	1.52123	YES	YES
19	a	281.67	4.63536	YES	YES
20	a	298.09	0.63321	YES	YES
21	a	319.13	11.57176	YES	YES
22	a	373.67	2.49350	YES	YES
23	a	419.24	0.02104	YES	YES
24	a	435.64	1.37615	YES	YES
25	a	451.47	20.52725	YES	YES
26	a	466.16	32.26420	YES	YES

27	a	489.32	0.55905	YES	YES
28	a	502.62	22.65035	YES	YES
29	a	525.04	3.57576	YES	YES
30	a	556.18	0.51278	YES	YES
31	a	567.95	24.67162	YES	YES
32	a	625.30	3.33877	YES	YES
33	a	666.70	11.00027	YES	YES
34	a	671.20	4.87135	YES	YES
35	a	719.36	49.34525	YES	YES
36	a	745.64	1.49321	YES	YES
37	a	782.67	8.79822	YES	YES
38	a	784.67	35.35515	YES	YES
39	a	789.05	12.34079	YES	YES
40	a	802.39	6.28426	YES	YES
41	a	823.58	27.52385	YES	YES
42	a	865.78	62.78957	YES	YES
43	a	877.29	3.40879	YES	YES
44	a	904.35	5.67500	YES	YES
45	a	935.10	4.61926	YES	YES
46	a	964.91	11.31828	YES	YES
47	a	978.12	18.16603	YES	YES
48	a	996.80	3.34152	YES	YES
49	a	1033.99	36.26383	YES	YES

50	a	1071.52	9.41117	YES	YES
51	a	1082.73	0.02608	YES	YES
52	a	1098.91	139.20555	YES	YES
53	a	1104.29	31.09739	YES	YES
54	a	1151.98	281.06179	YES	YES
55	a	1167.28	4.28931	YES	YES
56	a	1197.35	145.61736	YES	YES
57	a	1210.36	83.02230	YES	YES
58	a	1230.17	42.28331	YES	YES
59	a	1282.28	92.52058	YES	YES
60	a	1298.95	464.44994	YES	YES
61	a	1315.25	67.44838	YES	YES
62	a	1332.37	135.65830	YES	YES
63	a	1361.96	23.10684	YES	YES
64	a	1373.84	385.35601	YES	YES
65	a	1381.85	18.06730	YES	YES
66	a	1387.22	15.84337	YES	YES
67	a	1393.01	64.92003	YES	YES
68	a	1406.02	2.40237	YES	YES
69	a	1445.61	4.91938	YES	YES
70	a	1449.30	259.86756	YES	YES
71	a	1452.33	11.74780	YES	YES
72	a	1453.44	15.88410	YES	YES

73	a	1465.08	271.12370	YES	YES
74	a	1473.16	20.61703	YES	YES
75	a	1492.63	22.98740	YES	YES
76	a	1513.15	351.22153	YES	YES
77	a	1548.21	1251.44629	YES	YES
78	a	1576.94	88.49875	YES	YES
79	a	1627.66	1454.69493	YES	YES
80	a	1668.34	1427.72871	YES	YES
81	a	1795.80	935.58818	YES	YES
82	a	2338.03	496.77366	YES	YES
83	a	3035.28	8.05020	YES	YES
84	a	3037.64	36.25838	YES	YES
85	a	3060.75	32.50772	YES	YES
86	a	3065.87	97.68410	YES	YES
87	a	3106.98	1.30561	YES	YES
88	a	3113.06	0.50999	YES	YES
89	a	3120.98	41.34260	YES	YES
90	a	3123.11	69.25046	YES	YES
91	a	3128.53	18.43505	YES	YES
92	a	3134.62	63.75537	YES	YES
93	a	3191.44	4.16186	YES	YES
94	a	3196.57	0.81924	YES	YES
95	a	3241.90	3.65567	YES	YES

96	a	3247.15	0.76106	YES	YES

Table S6. NBO analysis of DCCO

Atom No	Charge	Core	Valence	Rydberg	Total
1 o	-0.54087	1.99958	6.53072	0.01057	8.54087
2 o	-0.63135	1.99972	6.61870	0.01293	8.63135
3 n	-0.17827	1.99923	5.15496	0.02408	7.17827
4 c	0.38652	1.99858	3.59039	0.02452	5.61348
5 c	-0.33581	1.99891	4.32098	0.01591	6.33581
6 c	0.23622	1.99893	3.74505	0.01980	5.76378
7 c	-0.28841	1.99895	4.27462	0.01484	6.28841
8 c	-0.16027	1.99894	4.14510	0.01623	6.16027
9 c	-0.18445	1.99881	4.17007	0.01558	6.18445
10 c	-0.10172	1.99893	4.08550	0.01729	6.10172
11 c	-0.24316	1.99879	4.22752	0.01685	6.24316
12 c	0.82952	1.99908	3.12301	0.04840	5.17048
13 c	0.03972	1.99920	3.92850	0.03258	5.96028
14 h	0.25027	0.00000	0.74591	0.00382	0.74973
15 h	0.24194	0.00000	0.75498	0.00307	0.75806
16 h	0.24359	0.00000	0.75352	0.00289	0.75641
17 h	0.24787	0.00000	0.74903	0.00309	0.75213
18 h	0.20315	0.00000	0.79048	0.00638	0.79685

19 n	-0.46242	1.99906	5.45166	0.01169	7.46242
20 c	-0.21277	1.99917	4.19657	0.01703	6.21277
21 c	-0.63806	1.99924	4.63139	0.00742	6.63806
22 h	0.22277	0.00000	0.77341	0.00382	0.77723
23 h	0.22663	0.00000	0.77075	0.00262	0.77337
24 h	0.21638	0.00000	0.78121	0.00240	0.78362
25 h	0.21566	0.00000	0.78164	0.00270	0.78434
26 h	0.23082	0.00000	0.76597	0.00321	0.76918
27 c	-0.21316	1.99917	4.19689	0.01710	6.21316
28 c	-0.63910	1.99924	4.63243	0.00743	6.63910
29 h	0.22258	0.00000	0.77355	0.00387	0.77742
30 h	0.22719	0.00000	0.77021	0.00260	0.77281
31 h	0.21568	0.00000	0.78163	0.00269	0.78432
32 h	0.21713	0.00000	0.78050	0.00236	0.78287
33 h	0.23091	0.00000	0.76589	0.00320	0.76909
34 o	-0.57403	1.99978	6.56221	0.01203	8.57403
35 h	0.49931	0.00000	0.49552	0.00518	0.50069

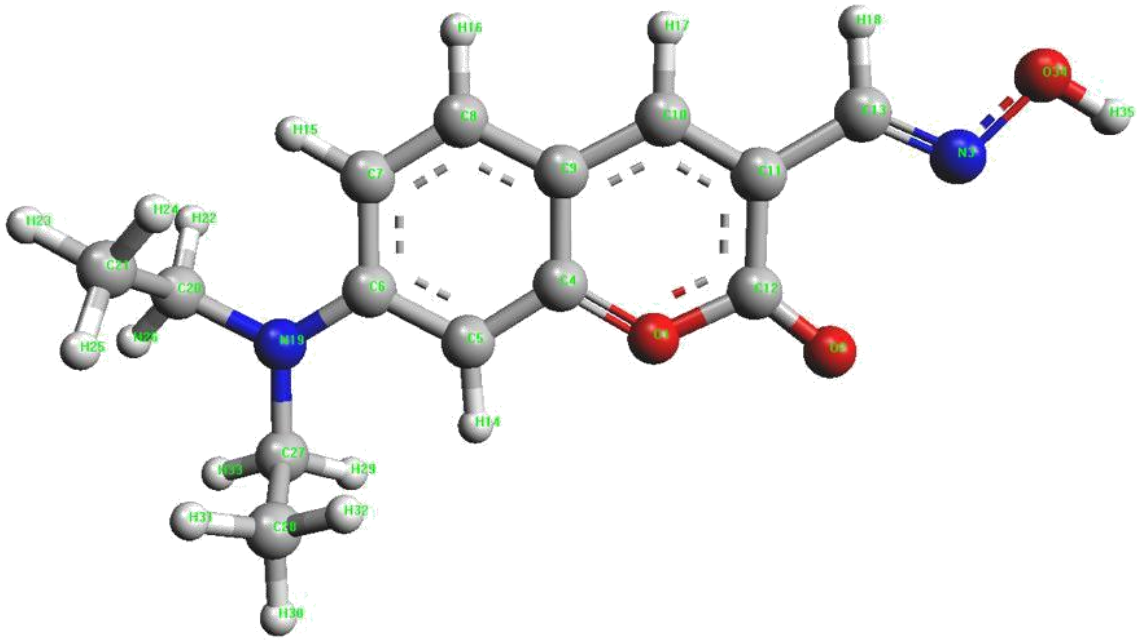


Fig. S16. Atom numbering scheme for DCCO.

Table S7. NBO analysis of DCC.

Atom No		Charge	Core	Valence	Rydberg	Total
1	o	-0.53225	1.99957	6.52199	0.01069	8.53225
2	o	-0.63914	1.99972	6.62656	0.01286	8.63914
3	c	0.39274	1.99857	3.58424	0.02445	5.60726
4	c	-0.33116	1.99891	4.31620	0.01605	6.33116
5	c	0.25004	1.99893	3.73109	0.01993	5.74996
6	c	-0.28272	1.99895	4.26890	0.01488	6.28272
7	c	-0.14946	1.99894	4.13418	0.01635	6.14946
8	c	-0.18748	1.99881	4.17299	0.01568	6.18748
9	c	-0.06018	1.99893	4.04443	0.01682	6.06018
10	c	-0.33522	1.99874	4.32209	0.01438	6.33522

11 c	0.84099	1.99910	3.11235	0.04756	5.15901
12 n	-0.44845	1.99906	5.43765	0.01175	7.44845
13 c	-0.21351	1.99917	4.19730	0.01704	6.21351
14 c	-0.63913	1.99924	4.63242	0.00747	6.63913
15 c	-0.21344	1.99917	4.19723	0.01704	6.21344
16 c	-0.63833	1.99924	4.63161	0.00748	6.63833
17 h	0.25391	0.00000	0.74233	0.00376	0.74609
18 h	0.24527	0.00000	0.75166	0.00307	0.75473
19 h	0.24788	0.00000	0.74925	0.00288	0.75212
20 h	0.26253	0.00000	0.73490	0.00258	0.73747
21 h	0.22493	0.00000	0.77127	0.00380	0.77507
22 h	0.22925	0.00000	0.76821	0.00254	0.77075
23 h	0.21786	0.00000	0.77978	0.00236	0.78214
24 h	0.21686	0.00000	0.78048	0.00266	0.78314
25 h	0.23307	0.00000	0.76375	0.00317	0.76693
26 h	0.22512	0.00000	0.77114	0.00374	0.77488
27 h	0.22884	0.00000	0.76862	0.00255	0.77116
28 h	0.21683	0.00000	0.78050	0.00267	0.78317
29 h	0.21729	0.00000	0.78032	0.00239	0.78271
30 h	0.23317	0.00000	0.76365	0.00318	0.76683
31 c	0.34387	1.99925	3.61814	0.03873	5.65613
32 n	-0.40999	1.99957	5.39039	0.02003	7.40999

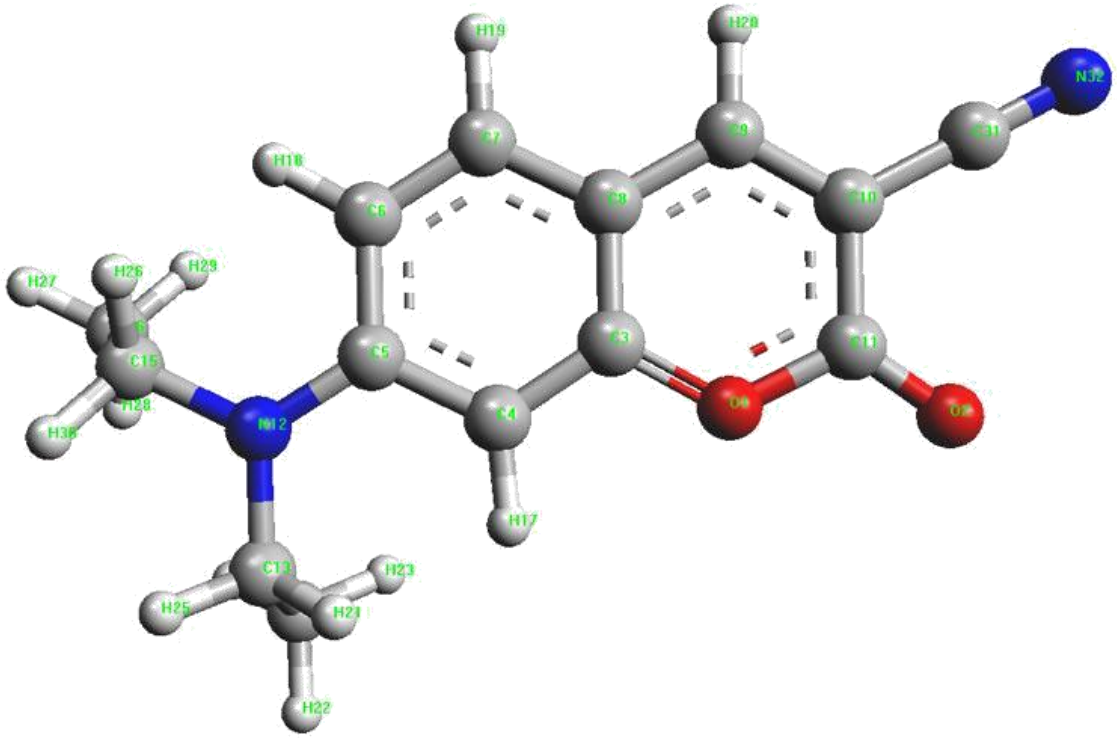
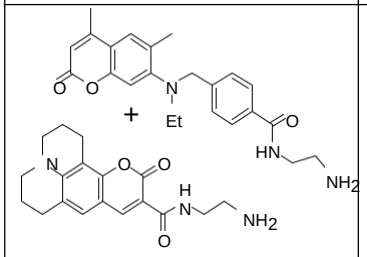
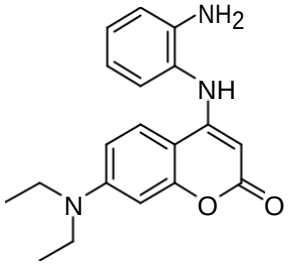
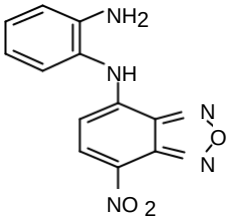
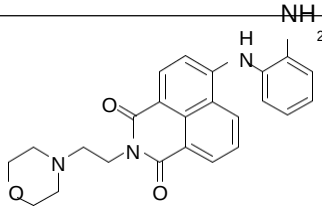
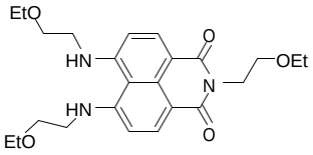
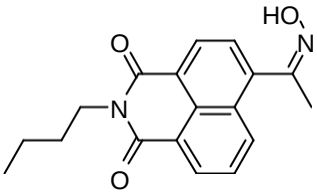
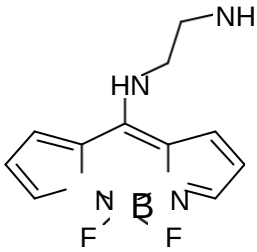
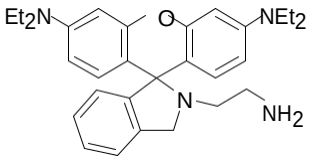
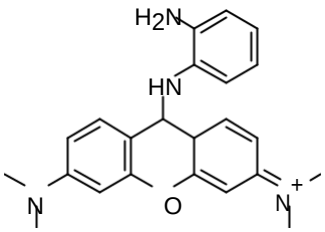
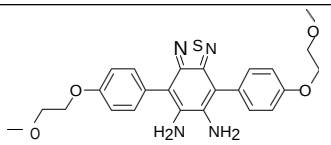
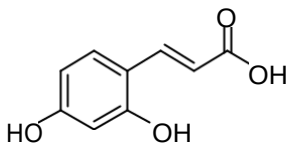
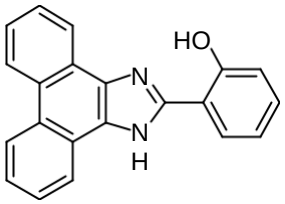
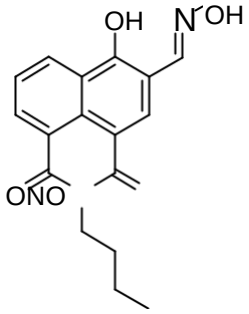
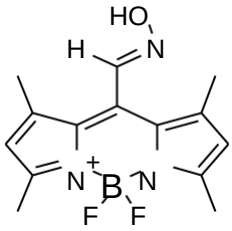
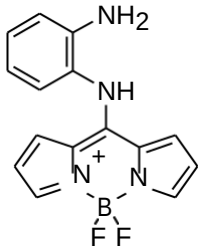
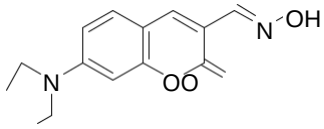


Fig. S17. Atom numbering scheme for DCC.

Table S8. Comparative table of previously reported probe with our sensor

Compound	Excitation (nm)/ Emission (nm)	Response time	Detection limit	Selectivity	Ref.
	343/464	Not calculated	No	Yes	Chem. Commun. 2007, 1238−1239
	368/446	< 30 sec.	3 nM & 10 ppm gas	Yes	ACS Sens. 2017, 2, 178−182
	270/315	150 sec	7 nm	Yes	ACS Appl. Mater. Interfaces 2016, 8, 22246−22252
	465/512	30 sec	2.8 ppb	Yes	ACS Appl. Mater. Interfaces 2016, 8, 22246−22252
	410/511	20 min	1.3 nM	Yes	Chem. Commun. 2017, 53, 1530−1533

	367/448	Not calculated	6.3 nM	Yes	Dyes and Pigments 173 (2020) 107854
		1.5 sec	0.12 nM	Yes	ACS Appl. Mater. Interfaces 2017, 9,13920−13927
	560/590	Not calculated	50 nM	Yes	Chem. Commun. 2012, 48, 1895−1897
	580/595	Several seconds	20 nM	Yes	Angew. Chem., Int. Ed. 2016, 55, 4729−4733
	380/508	20 min	20 nM	No	Org. Chem. Front. 2017, 4, 1719−1725
	330/382	Not calculated	1 nM	No	Anal. Chem. 2012, 84, 4594−4597.

	335/393	30 sec	0.14µM	Yes	Talanta, 2019, 200, 78-83
	382/577	< 1.5 sec in solution and < 5 sec in solid phase	0.09 nM	Yes	*J.Mater. Chem. A*, 2019,7, 1756-1767
	530/570	< 10 s	0.09 ppb	Yes	Anal. Chem. 2017, 89, 12837−12842
	450/530	15 sec	2.7 nM	5 min	Anal. Chem. 2017, 89, 4192−4197
	425/487	< 1 min	0.12 µM	Yes	This work