Electronic Supplementary Information

A rhodamine based fluorescent and colorimetric chemosensor for the detection of Cr^{3+} and its utility in molecular logic gate

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Figure Caption

Experiment

Procedure for Synthesis of Compound 4

Diethyl 2, 6-dimethyl-4-(4-nitrophenyl)-1, 4-dihydropyridine-3, 5-dicarboxylate (**1**, 2 g, 1 mmol) and selenium dioxide (740 mg, 2.5 mmol) were dissolved in 1, 4-dioxane in a round bottom flask. After the addition, the reaction mixture was refluxed for 10 mins. The reaction progress was monitored by thin layer chromatography. When reaction was completed then the reaction mixture was cooled at room temperature and then filtered to remove selenium. The obtained filtrate was then evaporated under reduced pressure to obtain the crude product. The desired pure aldehyde was then obtained by column chromatography (hexane: ethyl acetate, 7:3, v/v) in 59 % yield.

^{1}H NMR (400 MHz, DMSO-d_6): δ ppm 9.95 (s, 1H), 8.30 (d, J = 8.8 Hz, 2H), 7.47 (d, J = 8.8 Hz, 2H), 4.01 (m, J = 7.1, 2.2 Hz, 4H), 2.63 (s, 3H), 0.92 (t, J = 7.1 Hz, 3H), 0.85 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, DMSO-d_6): δ ppm 192.7, 166.0, 165.4, 157.2, 147.6, 144.7, 140.7, 130.4, 123.5, 62.5, 62.2, 22.5, 13.5. IR (KBr, cm^{-1}): 2895, 2860 and 1720. Melting Point: 130-132 ^{o}C. HRMS (m/z): Calculated for $C_{19}H_{18}N_2O_7$ 387.1148, obtained 387.1187.

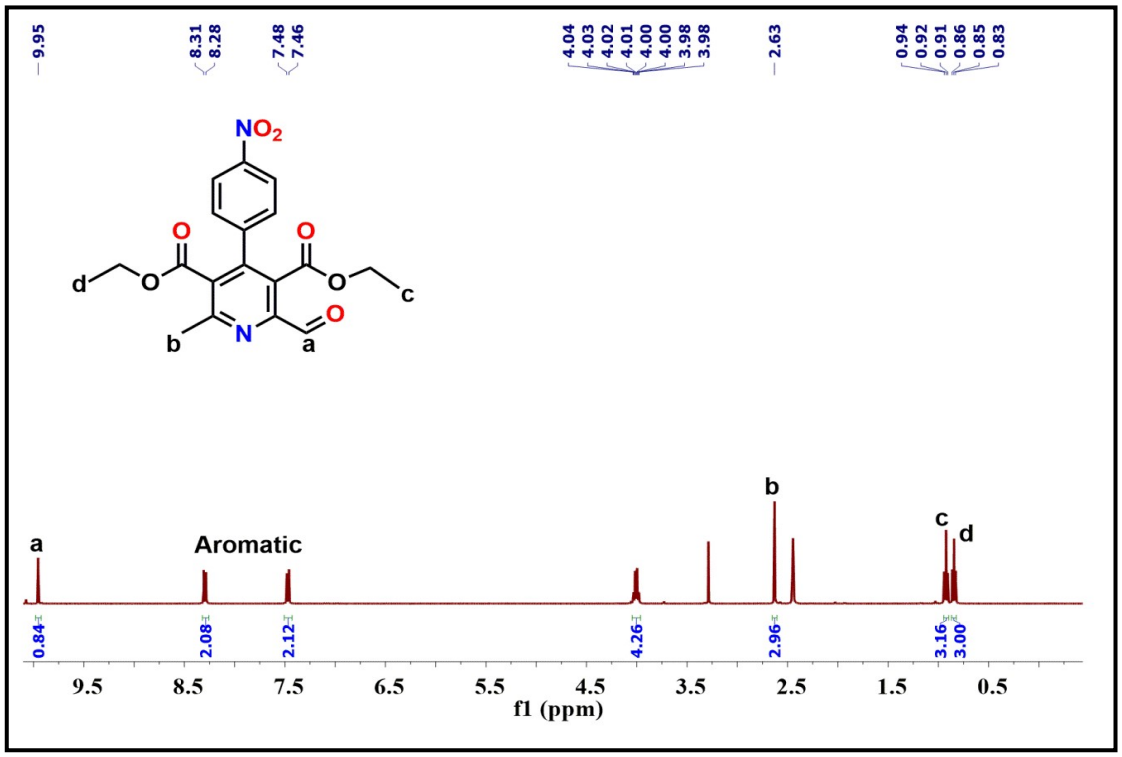


Figure 1: ^{1}H NMR of compound **4** in DMSO-d_6

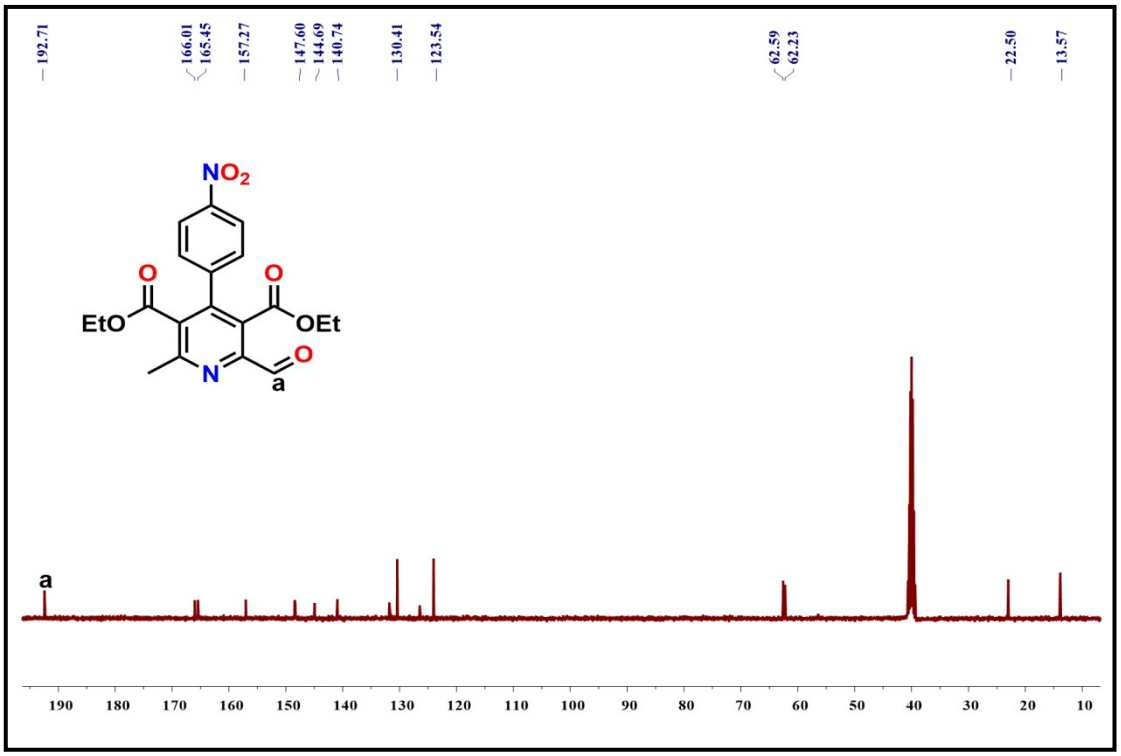


Figure 2: ^{13}C NMR of compound **4** in DMSO-d_6

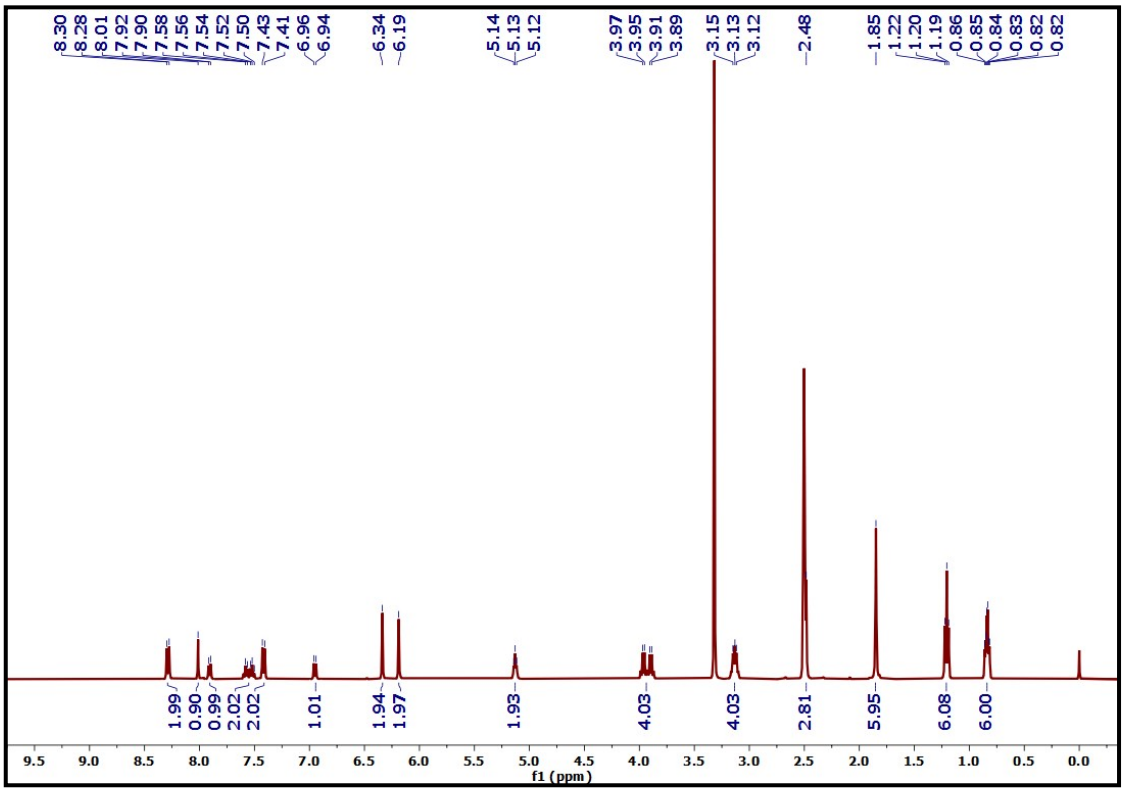


Figure 3: ^{1}H NMR of compound **S1** in DMSO-d_6

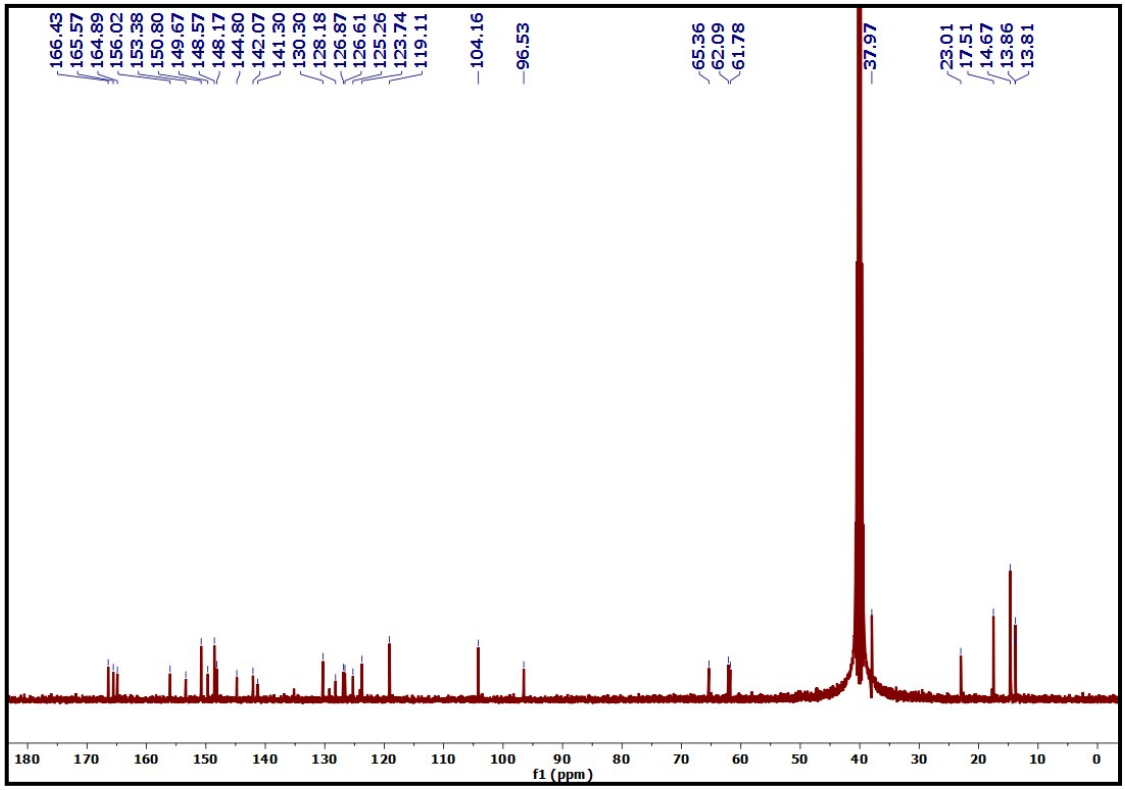
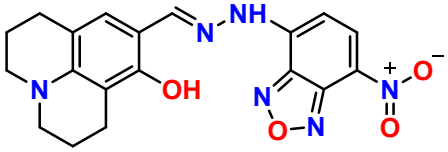
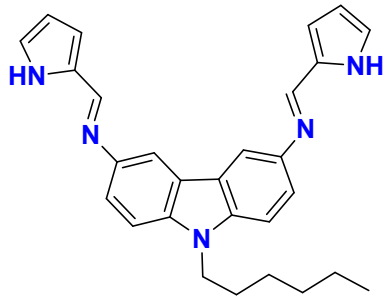
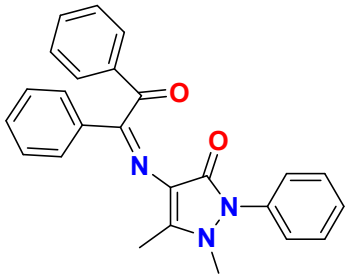
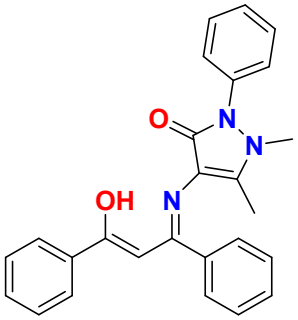
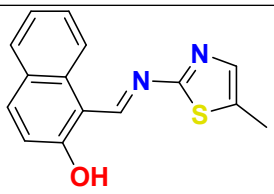
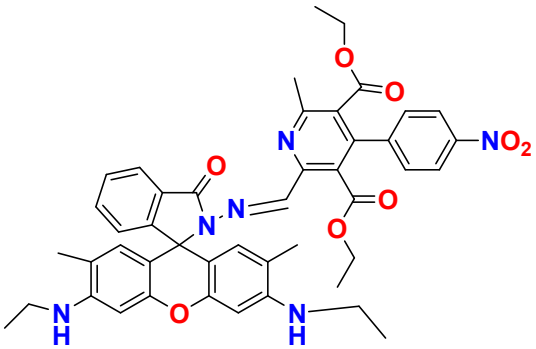


Figure 4: ^{13}C NMR of compound **S1** in DMSO-d_6

The chemosensor **S1** exhibit remarkably good sensing ability as compared to various literature reported chemosensors for detection of Cr^{3+} as shown in Table 1**.**

Table 1. The Sensing abilities of various chemosensors for Cr^{3+} ions reported in literature.

S.No.	Chemosensors	Detection Limit (in µM)	Ref.
1.		0.59	1

2.		1.08	2
3.		0.96	3
4.		1.21	4
5.		0.54	5
6.		0.21	Present Work

Single crystal X-ray diffraction analysis

Crystals of compound **S1** were grown by allowing slow evaporation of the saturated acetonitrile solvent at room temperature for SC-XRD studies. Good quality needle shaped colorless crystals were withdrawn and exposed to X-rays on a Bruker diffractometer employing a graphite

monochromatized Mo/Kα radiation (λ = 0.71073 Å) at temperature 273 K. The crystal data was reduced using CrysAlis pro software available with the diffractometer. Further, least square refinement after introduction of anisotropic displacement parameters yielded the R values mentioned in **Table 2**. The structure was solved by direct methods using SHELXT-2014 and refined by the full-matrix least-squares method on Olex2.refine 1.5. All calculations were carried out using the OLEX2 package of the crystallographic programs.[6] For the molecular graphics, the program Mercury (2022.3.0) was used. [7] The selected cell parameters, *etc.* are given in **Table 2.**

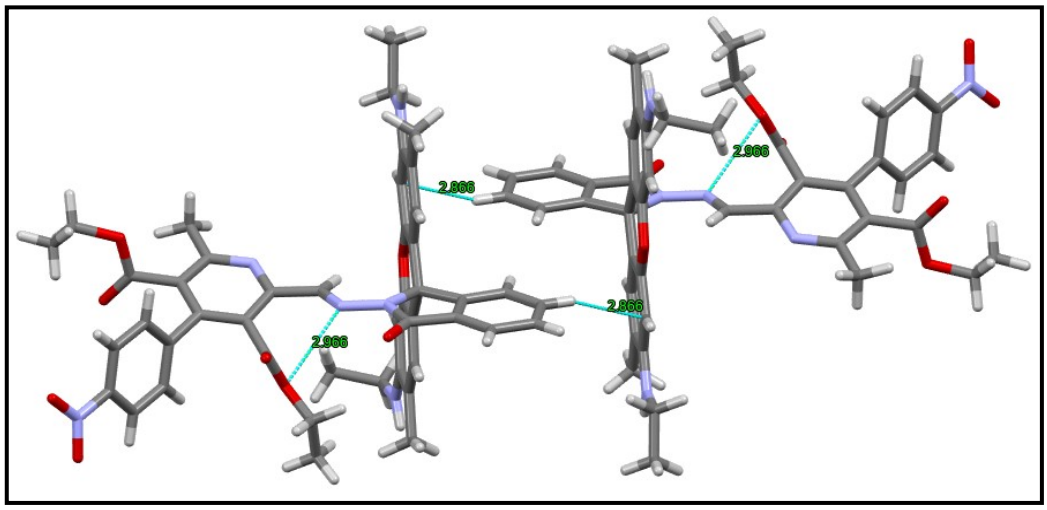


Figure 5:1D arrangement of **S1** *via* intra- and intermolecular non-covalent interactions between the adjacent molecules.

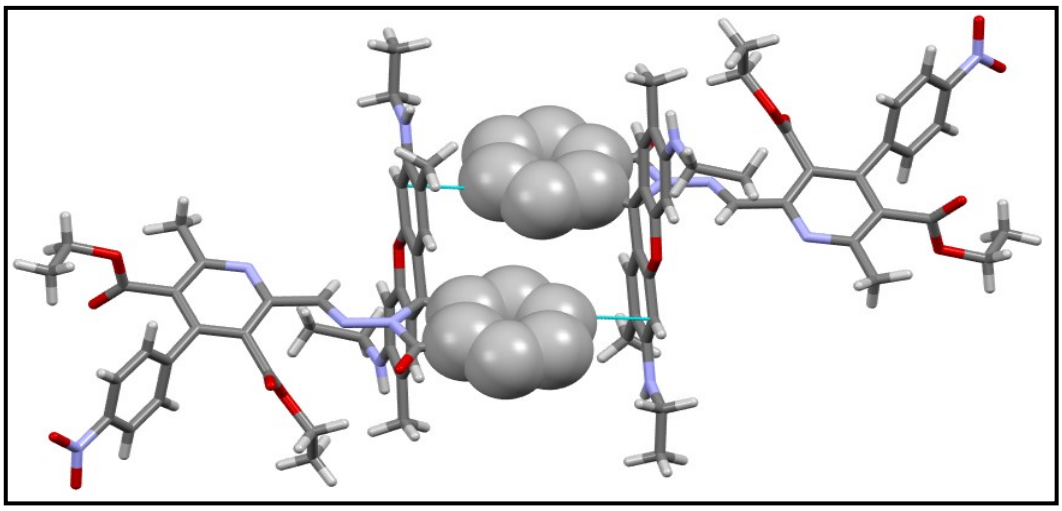


Figure 6: Double decker π-stacked arrangement of two phenolic rings and hydrogen bonding between the adjacent molecules.

Accession Codes

CCDC 2239138 contains the supplementary crystallographic data for ligand **S1** for this paper. This data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

Table 2. Crystal data and structure refinement for compound	
Identification code	**S1**
Empirical formula	$C_{45}H_{44}N_6O_8$
Temperature/K	273(2)
Crystal system	monoclinic
Space group	P-1
a/Å	9.2544(18)
b/Å	14.853(3)
c/Å	15.963(3)
α/°	86.399(6)
β/°	78.902(6)
γ/°	85.910(6)
Volume/Å^3	2144.9(7)
Z	43
ρ_{calc}/g cm^{-3}	1.432
μ/mm^{-1}	0.132
F(000)	946.927
Radiation	Mo/K_α (λ = 0.71073)
2θ range for data collection/°	2.25 to 28.35
Index ranges	$-12 \leq h \leq 12$, $-19 \leq k \leq 19$, $0 \leq l \leq 21$
No of Reflections measured	10680
Independent reflections	7068
Goodness-of-fit on F^2	1.081
R [$F^2 > 2\sigma(F^2)$], *wR*(all data)	0.0631, 0.2002

DFT Calculations of S1 and S1-Cr^{3+}

The simulated spectrum is depicted in **Figure 7**

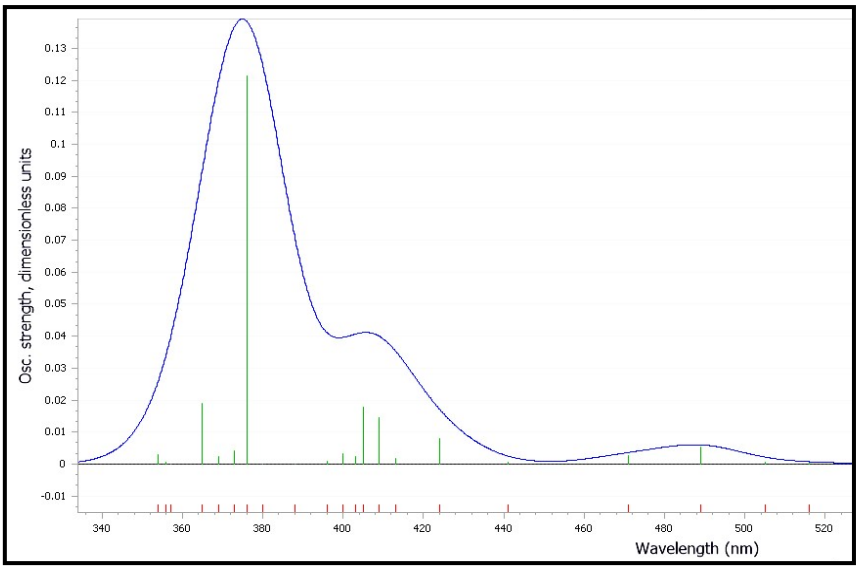


Figure 7: Predicted absorption spectrum of **S1**.

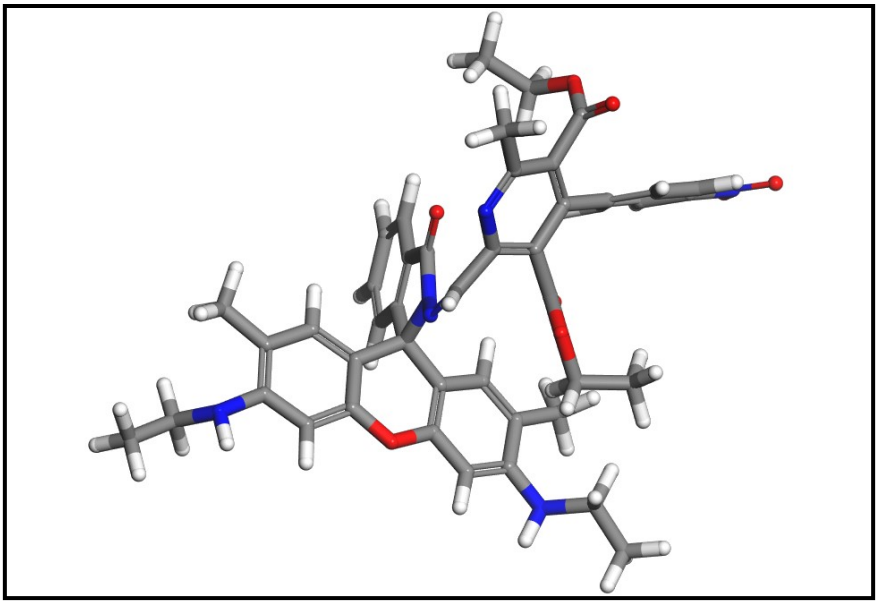


Figure 8: Optimized structure of **S1**

Final Coordinates (Angstroms)

	ATOM	X	Y	Z
1	C	-3.074714	-1.352920	-0.080309
2	C	-3.164308	-2.618486	0.506213
3	O	-2.120531	-3.524320	0.519334

4	C	-1.038521	-3.255076	-0.294024
5	C	-0.835394	-2.016764	-0.911071
6	C	-1.768359	-0.850511	-0.663042
7	C	-4.223310	-0.551964	-0.045042
8	C	-5.428205	-0.953301	0.529483
9	C	-5.494827	-2.254882	1.094695
10	C	-4.353672	-3.062909	1.080717
11	C	-0.139062	-4.305670	-0.479193
12	C	0.968407	-4.171192	-1.326739
13	C	1.163123	-2.945289	-2.018611
14	C	0.265260	-1.908126	-1.772544
15	C	-6.583200	0.006507	0.605867
16	N	-6.672129	-2.720493	1.718499
17	C	-7.861138	-2.957788	0.880125
18	C	-9.031158	-3.425762	1.734206
19	C	2.260214	-2.753665	-3.030281
20	N	1.829047	-5.272336	-1.533872
21	C	3.219941	-5.162540	-1.056904
22	C	4.017869	-6.407555	-1.415635
23	N	-1.126624	0.180639	0.272757
24	C	-1.185828	1.487302	-0.252889
25	C	-1.657038	1.336486	-1.641864
26	C	-1.976261	0.004681	-1.899224
27	C	-1.802472	2.325548	-2.614707
28	C	-2.266495	1.940268	-3.872523
29	C	-2.577544	0.597915	-4.137387
30	C	-2.434472	-0.384600	-3.152963
31	O	-0.930962	2.530126	0.350384
32	N	-1.096137	-0.175857	1.586294
33	C	-0.411569	0.463688	2.479088
34	C	0.563018	1.577120	2.391348
35	C	1.663255	1.569334	1.509102
36	C	2.429301	2.744324	1.392897
37	C	2.113203	3.821148	2.243164
38	C	1.123582	3.656165	3.234771
39	N	0.357232	2.559441	3.282684
40	C	0.894840	4.697072	4.294489
41	C	2.893403	5.102789	2.196285
42	O	2.683591	5.963135	1.162041
43	O	3.709246	5.394528	3.056942
44	C	1.550749	5.793705	0.255251
45	C	0.347030	6.568262	0.757050
46	C	3.573515	2.849123	0.448889
47	C	4.868587	3.073035	0.947248
48	C	5.955192	3.161928	0.082919
49	C	5.734463	3.041820	-1.288906
50	C	4.457052	2.840106	-1.814214
51	C	3.380434	2.738707	-0.940783
52	C	2.067679	0.314983	0.806225
53	O	2.347367	-0.644265	1.728747
54	O	2.166137	0.166294	-0.404328
55	C	2.749264	-1.944491	1.192407
56	C	4.226820	-1.962063	0.849507
57	N	6.877475	3.137308	-2.207964
58	O	8.007631	3.299452	-1.713976
59	O	6.648438	3.047392	-3.427926
60	H	-4.162142	0.456116	-0.460663
61	H	-4.379135	-4.069227	1.501392
62	H	-0.321971	-5.245303	0.044449
63	H	0.425620	-0.959145	-2.285356
64	H	-7.153594	-0.145554	1.534010
65	H	-6.224758	1.044621	0.585228
66	H	-7.286784	-0.109890	-0.236265
67	H	-6.468471	-3.565970	2.252026
68	H	-7.646538	-3.698166	0.083776
69	H	-8.124365	-2.019976	0.372836
70	H	-9.916902	-3.605399	1.109274
71	H	-8.795365	-4.368943	2.252070
72	H	-9.282822	-2.674397	2.494911
73	H	1.953301	-2.021229	-3.789345
74	H	3.185483	-2.367151	-2.570967
75	H	2.502357	-3.699876	-3.535012
76	H	1.410692	-6.115833	-1.140052
77	H	3.249348	-4.997047	0.039420
78	H	3.678374	-4.278300	-1.519367
79	H	5.048709	-6.322069	-1.044817
80	H	3.576585	-7.308309	-0.960185

81	H	4.045647	-6.556415	-2.503948
82	H	-1.552671	3.361513	-2.382666
83	H	-2.388348	2.686315	-4.659455
84	H	-2.938156	0.316505	-5.127406
85	H	-2.681779	-1.427285	-3.355865
86	H	-0.609344	0.111981	3.496993
87	H	0.011931	4.426160	4.883220
88	H	1.773070	4.769990	4.953923
89	H	0.750350	5.698023	3.860084
90	H	1.311699	4.730012	0.122138
91	H	1.914710	6.192350	-0.700943
92	H	-0.462790	6.521819	0.014650
93	H	-0.034286	6.136756	1.693058
94	H	0.604585	7.622564	0.930140
95	H	5.021299	3.168881	2.022032
96	H	6.966741	3.325580	0.449289
97	H	4.331414	2.760195	-2.892013
98	H	2.379228	2.556983	-1.328594
99	H	2.122202	-2.167012	0.320618
100	H	2.508707	-2.644409	2.003698
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103	H	4.838251	-1.695508	1.722883

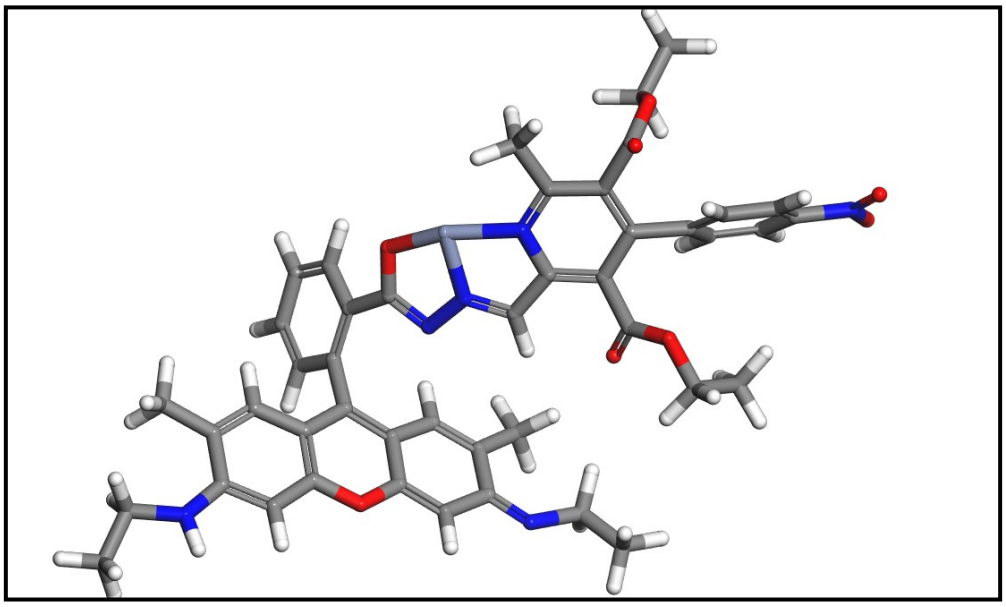

Figure 9: Optimized structure of **S1-Cr^{3+}**

Final Coordinates (Angstroms)

	ATOM	X	Y	Z
1	C	-4.670967	-2.263048	-0.332941
2	C	-4.461978	-3.528629	0.296297
3	O	-3.246356	-4.147235	0.248870
4	C	-2.255298	-3.639516	-0.560962
5	C	-2.445809	-2.424950	-1.294217
6	C	-3.639778	-1.694662	-1.127341
7	C	-5.960692	-1.687169	-0.160437

8	C	-7.017464	-2.315088	0.472892
9	C	-6.789278	-3.643018	1.012929
10	C	-5.477989	-4.187750	0.955268
11	C	-1.082811	-4.344603	-0.632291
12	C	0.017654	-3.901259	-1.461258
13	C	-0.224812	-2.740380	-2.346574
14	C	-1.408279	-2.054258	-2.204663
15	C	-8.330091	-1.582590	0.574263
16	N	-7.744557	-4.420125	1.585275
17	C	-9.213425	-4.308403	1.601103
18	C	-9.834533	-5.632861	2.025117
19	C	0.745486	-2.312765	-3.408609
20	N	1.113032	-4.609303	-1.299127
21	C	2.407779	-4.374403	-1.877210
22	C	3.476754	-5.192324	-1.154103
23	N	-1.496464	0.401337	-0.294086
24	C	-2.522207	1.199402	-0.533722
25	C	-3.538460	0.868338	-1.545526
26	C	-3.942318	-0.448112	-1.898437
27	C	-4.046362	1.962399	-2.278020
28	C	-4.892555	1.777059	-3.366560
29	C	-5.252114	0.482427	-3.745608
30	C	-4.795230	-0.608575	-3.001604
31	O	-2.543083	2.426369	0.011867
32	N	-0.591835	1.122436	0.451341
33	C	0.689262	0.738709	0.489291
34	C	1.565199	1.734350	1.007822
35	C	2.975935	1.677636	1.040837
36	C	3.698117	2.828860	1.420958
37	C	2.974412	3.946369	1.921572
38	C	1.575174	3.931535	1.937914
39	N	0.885064	2.873729	1.432187
40	C	0.750261	5.066861	2.471970
41	C	3.679670	5.091607	2.620284
42	O	4.143348	6.149323	1.942058
43	O	3.786003	5.030237	3.835553
44	C	3.969044	6.275391	0.485733
45	C	4.627765	7.574336	0.077618
46	C	5.166419	2.926414	1.213715
47	C	6.051065	3.271545	2.251734
48	C	7.413789	3.424865	1.991704
49	C	7.878479	3.233858	0.691901
50	C	7.028108	2.891621	-0.358535
51	C	5.669436	2.734695	-0.090467
52	C	3.641007	0.374012	0.667246
53	O	4.648691	0.091736	1.504134
54	O	3.243852	-0.344267	-0.245785
55	C	5.353798	-1.190394	1.282886
56	C	6.412420	-1.080088	0.202812
57	N	9.328783	3.399079	0.416235
58	O	10.045596	3.779238	1.348206
59	O	9.722866	3.138768	-0.727494
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61	H	-5.273124	-5.170948	1.381938
62	H	-0.937553	-5.249106	-0.041884
63	H	-1.587252	-1.181596	-2.834803
64	H	-8.712439	-1.558045	1.603895
65	H	-8.203312	-0.544971	0.242424
66	H	-9.107016	-2.034424	-0.058955
67	H	-7.403323	-5.307434	1.953523
68	H	-9.559873	-4.033829	0.595562
69	H	-9.520464	-3.510829	2.294264
70	H	-10.929179	-5.543788	2.013192
71	H	-9.560098	-6.445159	1.336414
72	H	-9.536476	-5.910823	3.047274
73	H	0.285797	-1.554775	-4.054867
74	H	1.665473	-1.881759	-2.984750
75	H	1.051690	-3.157199	-4.042410
76	H	2.673976	-3.301774	-1.863654
77	H	2.380784	-4.670014	-2.945594
78	H	4.461223	-5.021699	-1.610783
79	H	3.523366	-4.905207	-0.094214
80	H	3.247284	-6.264533	-1.206832
81	H	-3.735682	2.967197	-1.992334
82	H	-5.257681	2.638393	-3.925029
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84	H	-5.103515	-1.618748	-3.278008

85	H	-0.245103	4.712279	2.795287
86	H	1.216380	5.521769	3.357105
87	H	0.610877	5.862546	1.722897
88	H	2.890750	6.281822	0.266375
89	H	4.439509	5.409268	-0.003057
90	H	4.552350	7.700532	-1.011838
91	H	4.141353	8.433169	0.560388
92	H	5.690730	7.572482	0.353795
93	H	5.679884	3.407837	3.267602
94	H	8.113920	3.698007	2.781063
95	H	7.438704	2.760771	-1.359309
96	H	4.989228	2.480821	-0.906449
97	H	4.597660	-1.948422	1.044209
98	H	5.788598	-1.399368	2.267277
99	H	6.969672	-2.028754	0.165301
100	H	5.965871	-0.905979	-0.785480
101	H	7.128626	-0.277613	0.426107
102	Cr	-1.078920	2.803849	1.121002
103	H	1.014770	-0.196019	0.041079

Filter Paper strip application

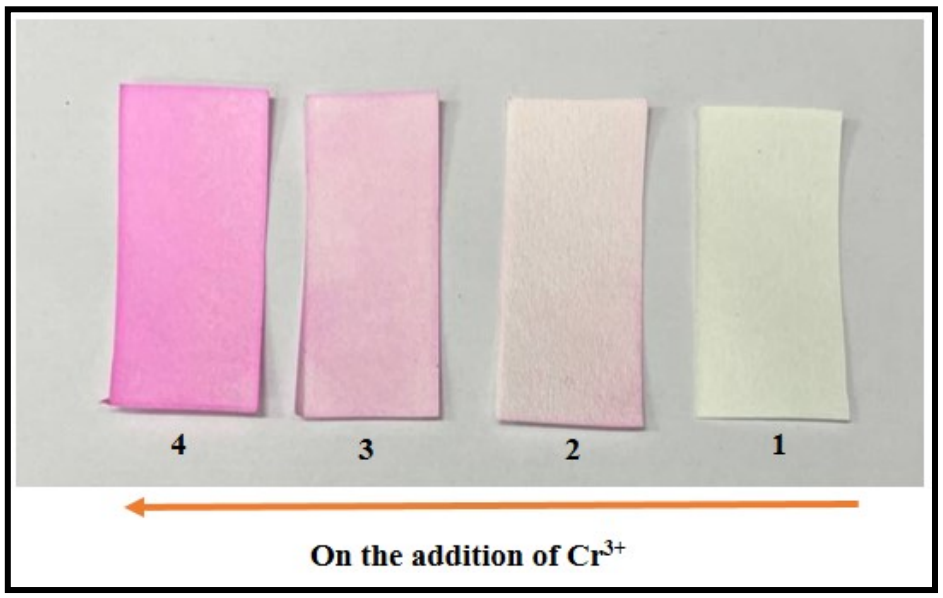

Figure 10: Paper strip test for **S1** with different concentration of Cr^{3+} under visible light (b) Filter paper strips coated with **S1**, paper -1 coated with **S1** only and filter paper 2,3,4 are coated with **S1** and further treated with 100µM, 10mM, 100mM of Cr^{3+} in water, respectively.

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