SUPPLEMENTARY INFORMATION (SI)

A *'turn-off'* emission based chemosensor for HSO_4^- - formation of a hydrogen-bonded complex

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S1. Experimental

1. General

Mass spectrum was recorded on UPLC-Q-TOF mass spectrometer. ^1H NMR and ^{13}C NMR spectra have been recorded on BRUKER Avance II 400 MHz and 100 MHz, respectively with TMS as internal standard using CD_3OD and $CDCl_3$ as deuterated solvent. Data are reported as follows: chemical shift in ppm (δ), integration, multiplicity (s=singlet, d=doublet, t=triplet, q=quartet, dd=double doublet), coupling constant J (Hz) and assignment. The purity of the solid products was checked by elemental analysis performed on Thermoelectron FLASH EA1112, CHNS analyzer. Stock solution of **1** (1 mM) was prepared using AR grade methanol. The UV-vis and fluorescence titration experiments were carried out by making dilution of the stock with methanol. Stock solution of anions (0.1M) were prepared by dissolving sodium salts of HSO_4^-, CH_3COO^-, HSO_3^-, SO_3^{2-}, SO_4^{2-}, F^-, Br^-, Cl^-, I^-, OH^-, citrate, HCO_3^-, CO_3^{2-}, CN^-, $H_2PO_4^-$, HPO_4^{2-}, PO_4^{3-}, NO_2^- and NO_3^- in distilled water. UV-visible spectral studies were conducted on Shimadzu 1601 PC spectrophotometer with a quartz cuvette (path length, 1cm). The absorption spectra have been recorded between 1100 and 200 nm. The cell holder of the spectrophotometer was thermostatted at 25°C for consistency in the recordings. The UV-vis titration experiment was performed by adding varying concentration of HSO_4^- (0-45 μM) to **1** (30 μM) in methanol. All the absorption spectra were recorded after equilibration of solution for 5 min. The steady state fluorescence experiments were carried out on Cary Eclipse spectrofluorometer at ambient temperature. A slit width of 5 nm was used with λ_{ex} = 320 nm and λ_{em} = 376 nm. The titration experiment was accomplished by varying the concentration of HSO_4^- (0-60 μM) and keeping the compound concentration constant (30µM). The working solution (30 µM) of **1** for fluorescence titration was prepared by making dilution of stock solution (1mM) with AR grade methanol.

2. Computational Methods

All theoretical calculations were carried out by using the Gaussian 09 suite of programs. The molecular geometry of **1** was optimized by DFT/B3LYP[1]/6-311G* method. The geometry of **1**:$NaHSO_4$ was optimized by DFT/MPW1PW91/GEN method in which 6-31G basis set was used for C and H and 6-311G** basis set was used for the donor atoms (N, Cl, O and S). Energy values and properties of the systems were computed at the same level and considering solvent (methanol) effects by using the Cossi and Barone's CPCM (conductor-like polarizable continuum model) modification[2] of the Tomasi's PCM formalism.[3] The first 20 excited states were calculated by using time-dependent density functional theory (TD-DFT) calculations. The molecular orbital contours were plotted using Gauss view 5.0.9.

3. Chemicals

Anions used in the spectrophotometric studies were added as sodium salts of analytical grade and bought from Sigma-Aldrich. The solvents used were also of analytical grade purchased from Thomas Baker.

4. Synthetic Procedure for 5-Ethoxycarbonyl-6-methyl-4-phenyl-2-[(7-chloroquinolin-4-ylamino) butylamino] pyrimidine (1) (Scheme 1).

To the stirred solution of 7-chloroquinyl-1,4-butandiamine [4] (1.1g, 4.41 mmol) in dry THF (50ml) mixture of 5-Ethoxycarbonyl-6-methyl-2-chloropyrimidines[5] (1g, 2.01mmol) and potassium carbonate (2.78g, 20.15 mmol) in dry THF was added. The reaction mixture was stirred for 48hrs at room temperature. Then, the reaction mixture was filtered and THF was removed under vacuum. The residue was purified by column chromatography using MeOH / EtOAc as eluent to give desired product. The product was recrystallized from DCM/ Hexane.

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[1] L. J. Bartolottiand, and K. Fluchick, *Reviews in Computational Chemistry* Lipkowitz, K. B.; Boyd, B. D. Eds., VCH, New York, 1996, **7**, 187.

[2] (a) V. Barone and M. Cossi, *J. Phys. Chem. A,* 1998, 102, 1995; (b) M. Cossi, N. Rega, G. Scalmani, V. J. Barone, *Comp. Chem.*, 2003, **24**, 669.

[3] S. Miertus, E. Scrocco and J. Tomasi, *J. Chem. Phys.* 1981, **55**, 117; (b) R. Cammi, B. Mennucci and J. Tomasi, *J. Phys. Chem., A* 2000, **104**, 5631.

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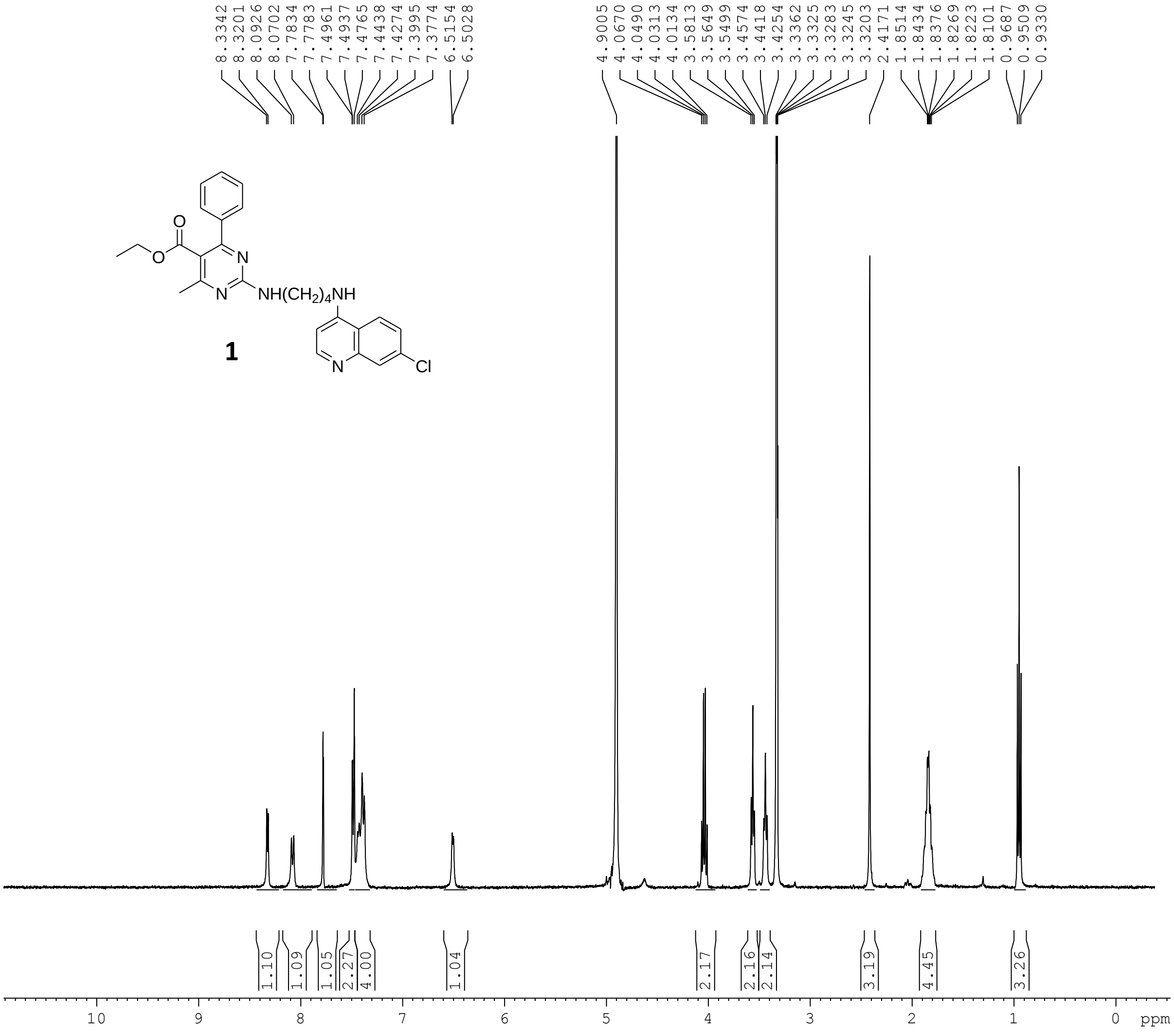
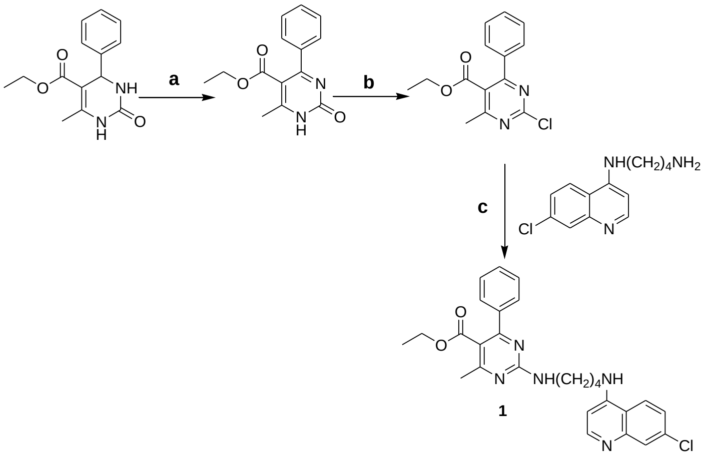
[5] (a) P. Biginelli, *Gazz. Chim. Ital.*, 1893, **23**, 360; (b) K. Singh and K. Singh, *Aust. J. Chem.*; 2008, **61**, 910; (c) K. Singh, K. Singh, B. Wan, S. Franzblau, K. Chibale and J. Balzarini, *Eur. J. Med. Chem.*; 2011, **46**, 2290.

White solid. Rf: 0.4 (EtOAc). Yield: 77%. IR (KBr): ν_{max}/ cm^{-1}. 3383 (NH), 2986 (C-H), 1708 (C=O), 1268(C-O). Found: C, 66.10; H, 5.63; N, 13.95. Calc. For $C_{27}H_{28}N_5O_2Cl$: C, 66.18; H, 5.72; N, 14.30%. ^{1}H NMR (400 MHz; CD_3OD; Me_4Si; ppm) δ_H: 0.95 (3H, t, *J* = 7.2 Hz, ester-CH_3), 1.81-1.85 (4H, m, CH_2), 2.41 (3H, s, C6-CH_3), 3.44 (2H, t, *J* = 6.6 Hz, CH_2), 3.56 (2H, q, *J* = 6.6 Hz, CH_2), 4.04 (2H, q, *J* = 7.2 Hz, ester-CH_2), 6.51 (1H, d, *J* = 5.0 Hz, ArH), 7.37-7.49 (6H, m, ArH), 7.78 (1H, d, *J* = 2.0 Hz, ArH), 8.08 (1H, d, *J* = 8.9 Hz, ArH), 8.33 (1H, d, *J* = 5.6 Hz, ArH) . ^{13}C NMR (75 MHz; $CDCl_3$; Me_4Si; ppm) δ_C: δ 13.5, 22.9, 25.8, 27.4, 40.6, 42.9, 61.1, 99.0, 115.4, 117.0, 120.8, 125.2, 127.8, 128.2, 128.7, 129.4, 134.8, 139.0, 149.0, 149.6, 151.9, 161.2, 168.7. *m/z* (EI): 490.1 (M^+).



1



Scheme 1. Reagents and conditions (a) Pyridinium chlorochromate, CH_2Cl_2, 24 hrs; (b) $POCl_3$, 105°C, 45 minutes; (c) THF, K_2CO_3, r.t, 48 hrs.

5. Calculation of Quantum Yield

Quantum yield of 1 and 1:HSO_4^- was calculated using formula:

$\Phi_u = \Phi_S I_u A_s/I_s A_u$

Where,

Φ_S is Quantum yield of standard;

I_u, I_s are Integrated Fluorescence of standard and unknown respectively;

A_S, A_u are absorbance of standard and unknown respectively

Quinine sulphate was used as standard whose quantum yield is 0.55 in 0.1N H_2SO_4 at λ_{ex}= 320 nm.[6]

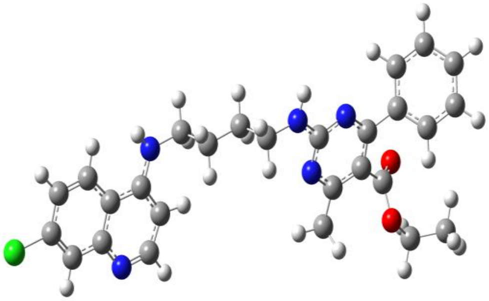


Fig. S1 Optimized structure of **1** using Gaussian 09 program (DFT/B3LYP/6-311G* method; Color codes; blue: N, red: O, green: Cl, Grey: C, white: H).

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[6] Y. Li, H. Chong, X. Meng, S. Wang, M. Zhu, and Q. Guo, *Dalton Trans.*, 2012, **41**, 6189- 6194.

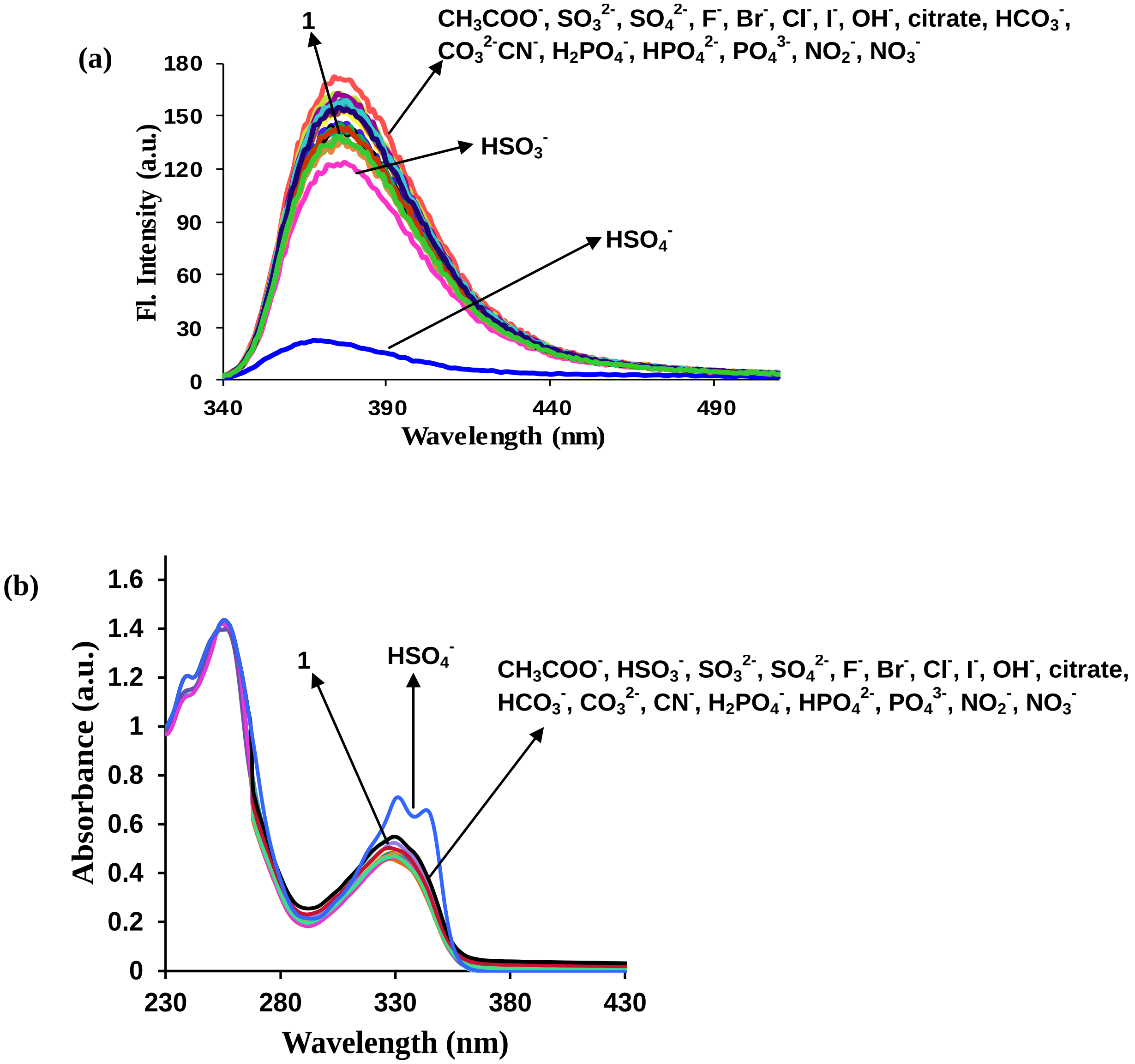


Fig. S2 (a) Emission spectra ; (b) absorption spectra of **1** (30 μM) in CH_3OH in the presence of various anions (80 μM) in distilled H_2O.

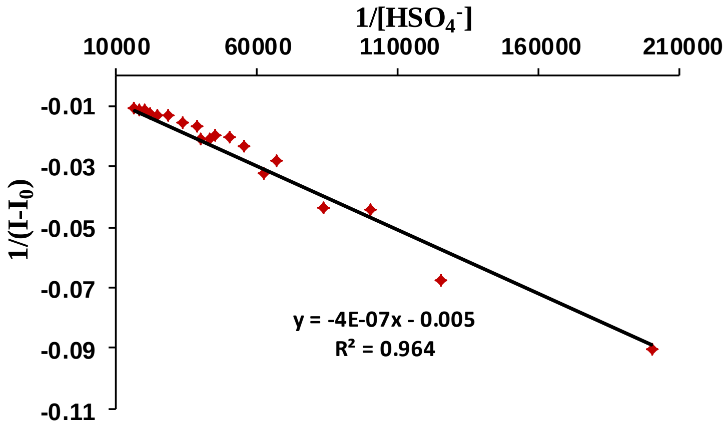


Fig. S3 Plot of $1/(I-I_0)$ vs $1/[HSO_4^-]$. Binding constant K is given by ratio of intercept to slope of graph i.e. K= Intercept/ Slope.

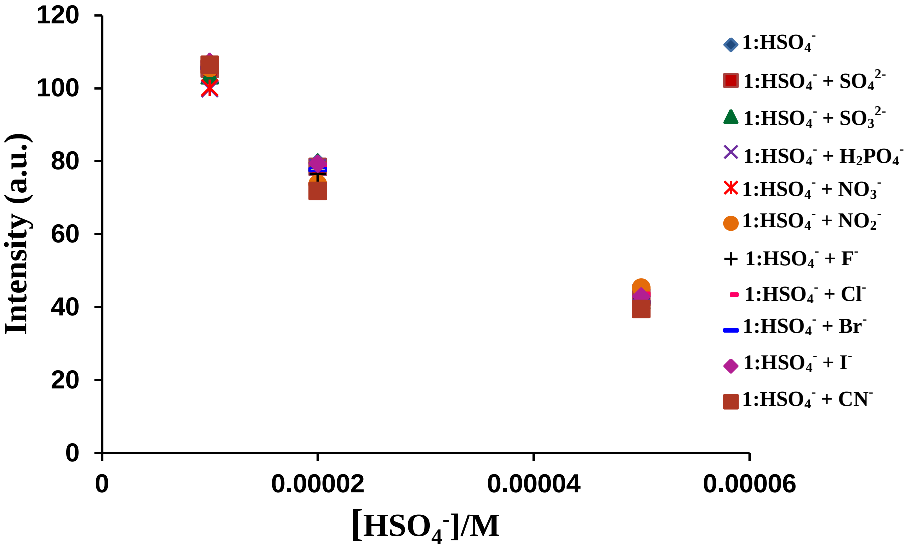


Fig. S4 Changes in the fluorescence intensity of **1** (30 µM) in CH_3OH at 376 nm upon titration with increasing concentration of HSO_4^- (10, 20 and 50 µM) in distilled H_2O, in the presence of other anions (60 µM) in distilled H_2O.

Table S1: Standard deviation in change in fluorescence intensity in the titration of **1** (30μM) with various anions (80μM).

Solution	Fluorescence intensity[a]	σ [b]
1	135.4948	0.1393
1 + CH_3COO^-	152.7754	0.0891
1 + HCO_3^-	171.7745	0.3068
1 + HSO_4^-	22.62011	0.1870
1 + HSO_3^-	121.3585	0.5154
1 + Br^-	145.5111	0.3189
1 + Cl^-	141.2891	0.4662
1 + citrate	163.2116	0.1162
1 + CO_3^{2-}	158.8271	0.0856
1 + CN^-	154.5972	0.5515
1 + $H_2PO_4^-$	136.2922	0.2094
1 + F^-	145.4497	0.5203
1 + OH^-	154.2522	0.4949
1 + I^-	135.2464	0.2292
1 + NO_3^-	137.5089	0.2031
1 + NO_2^-	145.5863	0.2791
1 + HPO_4^{2-}	161.9287	0.1414
1 + PO_4^{3-}	157.4484	0.5656
1 + SO_4^{2-}	143.4693	0.0802
1 + SO_3^{2-}	155.0231	0.2654

[a] *mean fluorescence intensity at 376 nm which is determined from three repeated experiments;* [b]*standard deviation.*

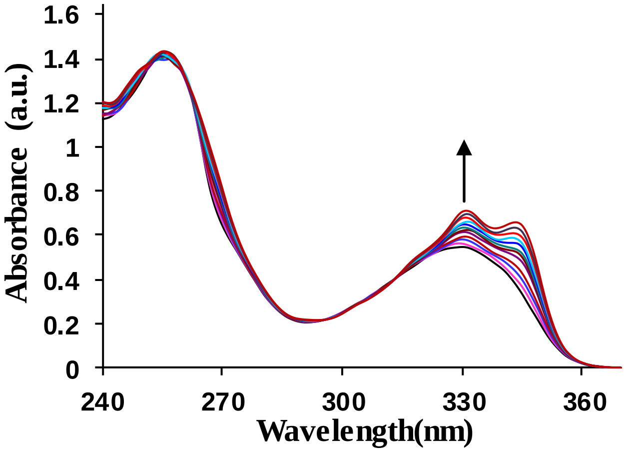


Fig. S5. UV/ vis spectra of **1** (30 μM) in CH_3OH titrated with HSO_4^- (0-1.5 equiv.) in distilled H_2O.

Table S2: (a) Selected data of electronic transitions in **1** by TDDFT method at the B3LYP/6-311G* level.[a][b]

State	λ [nm (eV)]	f	Composition of band and CI coefficiencies
1	319.24 (3.88)	0.1529	H→L, 0.14; H→ L+1, 0.67
12	250.43 (4.95)	0.4974	H→L+3, 0.19; H-2→L+2,0.27; H-4→L+2,0.24; H-4→L, 0.16; H-7→L+3,0.10

[a] Calculations were carried out for the lowest 50 excited states, and only energies above 240 nm with f > 0.15 are shown. [b] f = oscillator strength; CI = configuration interaction; H = HOMO; L = LUMO.

(b) Cartesian coordinates from the optimized structure of **1** at B3LYP/6-311G*

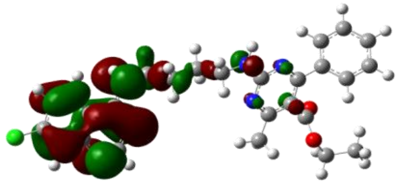
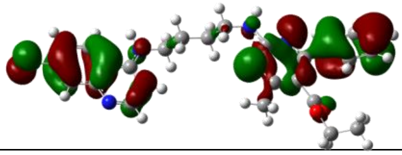
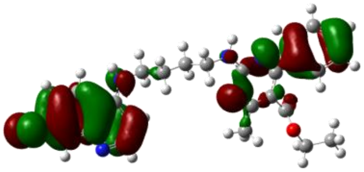
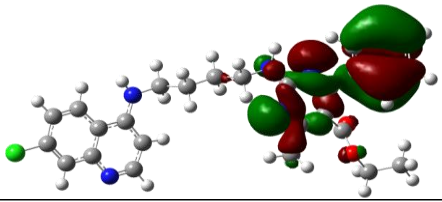
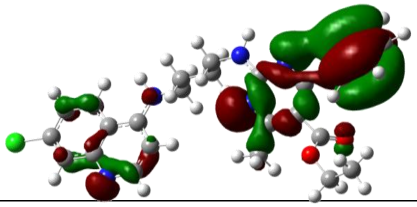
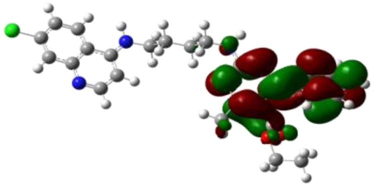
E = -1930.54a.u.

Center Number	**Atomic Number**	**Atomic Type**	**Coordinates (Å) X**	**Y**	**Z**
1	6	0	2.964919	0.977070	-0.342418
2	6	0	4.306651	0.646077	-0.069131
3	6	0	4.656640	-0.719343	-0.171578
4	6	0	2.488478	-1.229316	-0.680556
5	7	0	2.061543	0.043895	-0.645526
6	7	0	3.747306	-1.647862	-0.463391
7	6	0	6.047798	-1.222114	-0.012083
8	6	0	7.136821	-0.546195	-0.573430
9	6	0	6.272742	-2.432946	0.652973
10	6	0	8.424070	-1.062361	-0.460207
11	6	0	7.561472	-2.938930	0.782284
12	6	0	8.641443	-2.255638	0.225308
13	1	0	9.257354	-0.533896	-0.912068
14	1	0	7.723555	-3.870702	1.314761
15	1	0	9.646569	-2.654049	0.320067
16	6	0	5.263769	1.660922	0.462164
17	8	0	5.870544	1.554062	1.499292
18	8	0	5.356345	2.742968	-0.349829
19	6	0	6.175258	3.844216	0.120072

20	6	0	7.630752	3.665535	-0.275021
21	1	0	6.066995	3.923732	1.202104
22	1	0	8.063105	2.794767	0.219996
23	1	0	7.729429	3.544348	-1.356602
24	1	0	8.207993	4.546313	0.021197
25	6	0	0.169514	-1.971485	-1.212972
26	6	0	-0.671402	-1.953584	0.071033
27	1	0	0.061879	-1.020696	-1.737347
28	1	0	-0.185024	-2.757766	-1.886756
29	6	0	-2.158042	-1.713516	-0.206136
30	1	0	-0.535104	-2.902814	0.604285
31	1	0	-0.280061	-1.168241	0.726130
32	1	0	-2.290613	-0.764250	-0.735535
33	1	0	-2.547308	-2.492571	-0.873978
34	7	0	1.585056	-2.198089	-0.980736
35	1	0	1.949985	-3.136951	-0.966775
36	6	0	-2.998154	-1.701163	1.080252
37	1	0	-2.615706	-0.951417	1.778363
38	1	0	-2.901731	-2.662762	1.593563
39	7	0	-4.420330	-1.465005	0.880816
40	1	0	-4.954200	-2.266922	0.590594
41	6	0	-4.980302	-0.237642	0.637326
42	6	0	-6.391431	-0.127457	0.360176
43	6	0	-4.254445	0.947899	0.678070
44	6	0	-7.277121	-1.231993	0.333535

45	6	0	-6.921942	1.175770	0.111354
46	6	0	-4.901966	2.171148	0.435373
47	1	0	-3.191231	0.952411	0.880469
48	6	0	-8.613916	-1.078945	0.049567
49	1	0	-6.924695	-2.231587	0.566663
50	6	0	-8.302228	1.313302	-0.186015
51	1	0	-4.313701	3.086920	0.469202
52	6	0	-9.114074	0.210353	-0.217956
53	1	0	-9.282003	-1.931175	0.037660
54	1	0	-8.679157	2.309589	-0.377421
55	7	0	-6.178148	2.317271	0.149076
56	17	0	-10.826187	0.389248	-0.586561
57	6	0	2.442040	2.388768	-0.274466
58	1	0	2.874743	3.001565	-1.067547
59	1	0	1.358951	2.372923	-0.384078
60	1	0	2.698463	2.868714	0.673674
61	1	0	5.426617	-2.968551	1.066583
62	1	0	6.975995	0.373972	-1.125033
63	1	0	5.736938	4.723582	-0.353125

(c) Frontier orbitals of 1

Orbital	Electron density	Energy (eV)
HOMO(H)		-5.93
H-2		-6.98
H-3		-7.00
H-4		-7.15
H-5		-7.29
LUMO(L)		-1.64

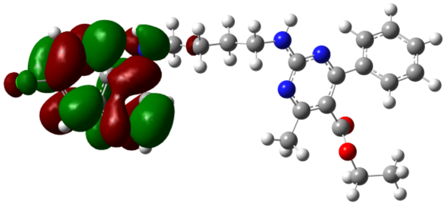
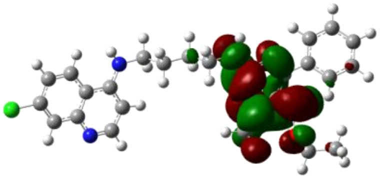
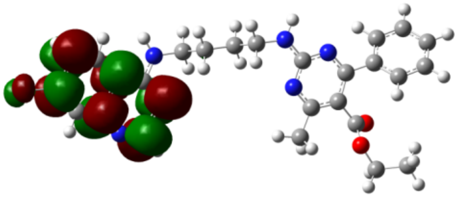
L+1		-1.55
L+2		-1.03
L+3		-0.86

Table S3: (a)Selected data of electronic transitions in **1:NaHSO$_4$** by TDDFT method at the B3LYP/GEN level.[a][b]

State	**λ [nm (eV)]**	**f**	**Composition of band and CI coefficiencies**
1	305.41 (4.06)	0.2046	H→L+1, 0.68
6	265.03 (4.68)	0.3043	H-1→L, 0.15; H-1→L+1, 0.20; H-1→L+2, 0.54; H→L+2, -0.31
12	242.31 (5.11)	0.3608	H-5→L, 0.31; H-5→L+2, 0.36; H-4→L+2, 0.25; H-2→L, -0.26; H-2→L+2, 0.22; H-1→L+2, -0.13

[a] Calculations were carried out for the lowest 20 excited states, and only energies above 240 nm with f > 0.19 are shown. [b] f = oscillator strength; CI = configuration interaction; H = HOMO; L = LUMO.

(b) Cartesian coordinates from the optimized structure of **1**:NaHSO$_4$ at MPW1PW91/GEN.

E= -2791.72 a.u.

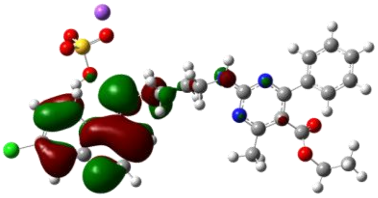
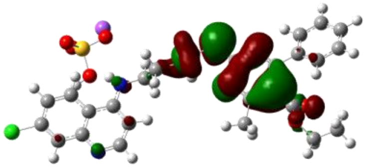
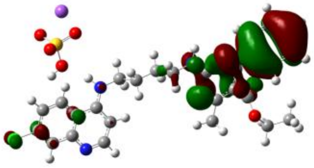
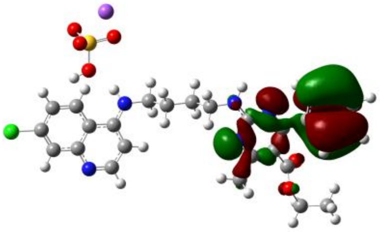
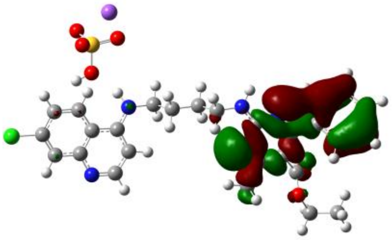
Center	Atomic		Forces (Hartrees/Bohr)	
Number	Number	X	Y	Z
1	6	-0.000000296	0.000000938	-0.000000349
2	6	-0.000000050	0.000001157	0.000000161
3	6	0.000000048	0.000000969	0.000000766
4	6	0.000000371	0.000000765	0.000000503
5	7	-0.000000398	0.000000750	-0.000000035
6	7	0.000000263	0.000001429	0.000000705
7	6	0.000000534	0.000001367	0.000000973

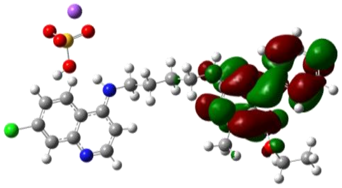
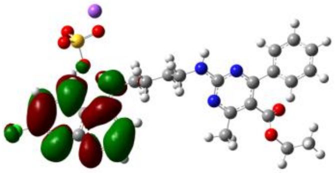
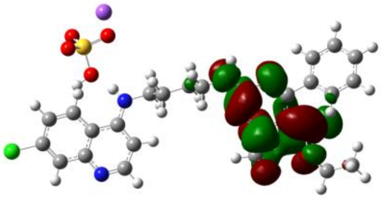
8	6	0.000000075	0.000001775	0.000000701
9	6	0.000000690	0.000001613	0.000001586
10	6	0.000000348	0.000002117	0.000001091
11	6	0.000000700	0.000001775	0.000001893
12	6	0.000000628	0.000001880	0.000001651
13	1	0.000000266	0.000002410	0.000000936
14	1	0.000001102	0.000001645	0.000002353
15	1	0.000000836	0.000002241	0.000001969
16	6	0.000000087	-0.000000144	-0.000001103
17	8	-0.000000137	0.000000756	0.000000536
18	8	-0.000000471	0.000001479	-0.000000475
19	6	-0.000000460	0.000000797	-0.000000990
20	6	-0.000000523	0.000001216	-0.000000762
21	1	-0.000000513	0.000000298	-0.000000736
22	1	-0.000000346	0.000001335	-0.000000263
23	1	-0.000000665	0.000001798	-0.000000780
24	1	-0.000000670	0.000001194	-0.000000926
25	6	0.000000050	0.000000853	0.000000360
26	6	0.000000273	0.000000221	0.000000473
27	1	-0.000000139	0.000000976	-0.000000070
28	1	0.000000169	0.000001170	0.000000541
29	6	0.000000070	-0.000000057	0.000000090
30	1	0.000000481	0.000000062	0.000000871
31	1	0.000000132	-0.000000132	0.000000282
32	1	-0.000000207	0.000000080	-0.000000297

33	1	0.000000157	0.000000219	0.000000327
34	7	0.000000263	0.000001155	0.000000648
35	1	0.000000411	0.000001327	0.000001051
36	6	0.000000220	-0.000000725	0.000000209
37	1	0.000000123	-0.000001067	0.000000048
38	1	0.000000447	-0.000000847	0.000000643
39	7	0.000000176	-0.000001141	-0.000000116
40	1	0.000000166	-0.000001237	0.000000204
41	6	-0.000000240	-0.000001147	-0.000000715
42	6	-0.000000373	-0.000001412	-0.000000857
43	6	-0.000000360	-0.000000871	-0.000001046
44	6	-0.000000160	-0.000001317	-0.000000488
45	6	-0.000000722	-0.000001545	-0.000001414
46	6	-0.000000463	-0.000001448	-0.000001590
47	1	-0.000000432	-0.000000872	-0.000000871
48	6	-0.000000112	-0.000001821	-0.000000752
49	1	0.000000082	-0.000001146	-0.000000176
50	6	-0.000000664	-0.000001800	-0.000001755
51	1	-0.000000904	-0.000001268	-0.000001862
52	6	-0.000000533	-0.000001899	-0.000001384
53	1	-0.000000131	-0.000001639	-0.000000554
54	1	-0.000000930	-0.000002025	-0.000002126
55	7	-0.000000955	-0.000001581	-0.000001784
56	17	-0.000000658	-0.000002177	-0.000001651
57	6	-0.000000569	0.000000376	-0.000000870

58	1	-0.000000649	0.000000821	-0.000001127
59	1	-0.000000596	0.000000248	-0.000000994
60	1	-0.000000489	0.000000031	-0.000000942
61	1	0.000000870	0.000001145	0.000001701
62	1	-0.000000071	0.000001923	0.000000289
63	1	-0.000000893	0.000000844	-0.000001328
64	16	0.000000194	-0.000001813	0.000001254
65	8	0.000001099	-0.000002528	0.000001288
66	8	0.000000752	-0.000001556	0.000000929
67	8	0.000001253	-0.000001667	0.000001381
68	8	0.000000654	-0.000001947	0.000000431
69	1	0.000000363	-0.000002240	0.000000215
70	11	0.000001423	-0.000002086	0.000002127

(c) Frontier orbitals of 1:$NaHSO_4$

Orbital	Electron density	Energy (eV)
HOMO (H)		-6.09
H-1		-6.42
H-2		-7.17
H-4		-7.35
H-5		-7.53

LUMO (L)		-1.38
L+1		-1.33
L+2		-0.88

Complete Reference for Gaussian (Reference 10 in manuscript)

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