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

Supporting Information

Rapid naked eye sensing of fluoride using upper rim functionalized pentafluorophenyl hydrazone derivative of calix[4]arene

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S1: General Information:

All solvents were purchased from Qualigens. Calix[4]arene was procured from Chemfill. Pentafluoro phenylhy-drazine and tetrabutylammonium (TBA) salts of anions, were purchased from Alfa Aesar. All the chemicals were used without further purification. NMR experiments were performed on a Bruker 500 MHz spectrometer. Agilent technologies model G6564 QTOF instrument using the electrospray ionization method was used for mass spectral analysis. Fourier transform infrared spectra were rec-orded by the KBr pellet method using Bruker Vertex 70V spectro-photometer. Absorption studies were done using HPLC grade solvent on Varian Cary 4000. The concentration of R was kept constant at 10 μM [100 μL of dimethyl sulfoxide was used for dissolving R in acetonitrile, while the concentrations of the anion were varied from 10 to 500 μM.

S2 Synthesis and characterization of P_2:

A slurry of calix[4]arene, P_1 (3 g, 4.629 mmol), phenol 2.25 ml and $AlCl_3$ (3.258 g, 24.4 mmol) was stirred in 100 ml of toulene at 50 °C for 1hr in inert atmosphere. Then the reaction mixture was poured into a 200 ml of cold 0.2 N HCl solution. Toulene layer was collected and washed with water 2 times followed by drying over anhydrous Na_2SO_4. Then the solution was evaporated and the residue was treated with methanol to obtain product as precipitate. Pure product P_2 was obtained by recrystallization of the crude from $CHCl_3$ and MeOH. ^{1}H NMR (500 MHz; $CDCl_3$): δ 10.2 (s, 4H, ArOH); 7.05 (d, 8H, ArH), 6.71 (t, 4H, ArH), 4.25 (br, 4H $ArCH_2$), 3.55 (br, 4H $ArCH_2$) as given in Figure S01.

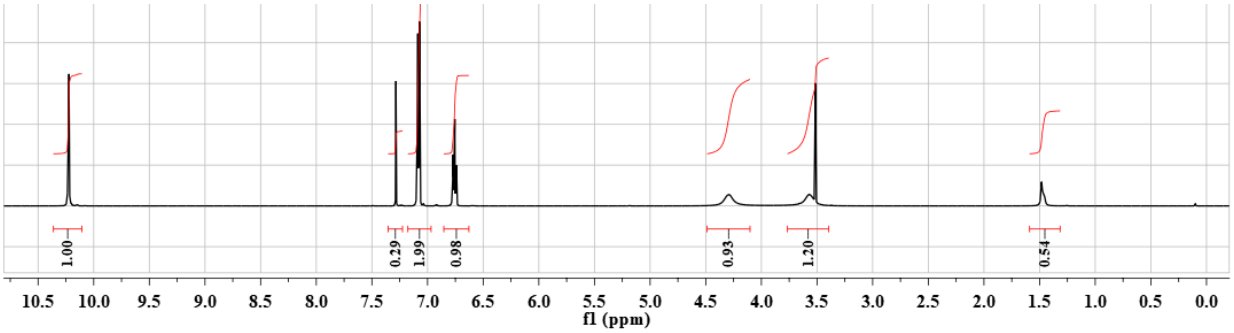


Figure S01 IH NMR spectrum of P_2 in $CDCl_3$.

S3 Synthesis and characterization of P_3:

A suspension of hexamethylene tetramine, HMTA (6 g, 42.8 mmol) and de-alkylated calix[4]arene, P_2 (0.5 g, 1.2 mmol) in 40 ml of trifluoroacetic acid was refluxed for 24 h. After cooling, the reaction mixture was poured into 1 N HCl (100 ml) solution and then stirred with dichloromethane (75 ml) for 6 h. Then the organic layer was separated and washed with water (2 × 50 ml) and the organic layer was dried over Na2SO4 and the solvent was evaporated in vacuum. Yield: 90%. ^{1}H NMR (500 MHz; DMSO-d^6): δ 9.6 (s, 4H, ArCHO), 7.65 (s, 8H, ArH) as shown in Figure S02.

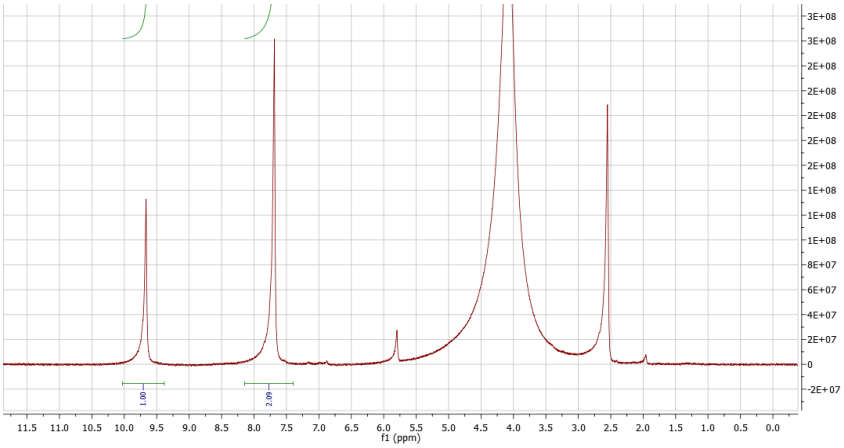


Figure S02 ^{1}H NMR spectrum of P_3 in DMSO-d^{6}.

S4 Characterization data of R:

The synthesis method and characterization data are given in the experimental section of the main manuscript. The ^{1}H, ^{13}C NMR, HRMS and FT-IR are given below.

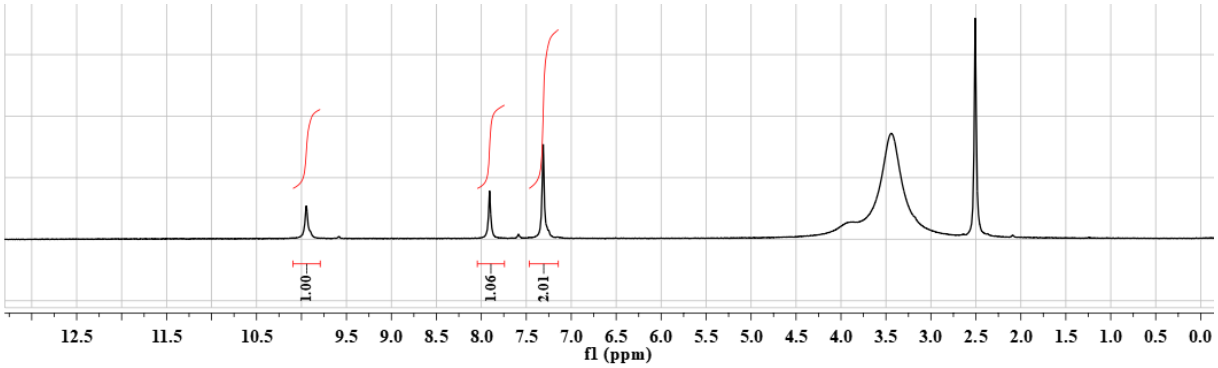


Figure S03 ^{1}H NMR spectrum of R in DMSO-d^{6}.

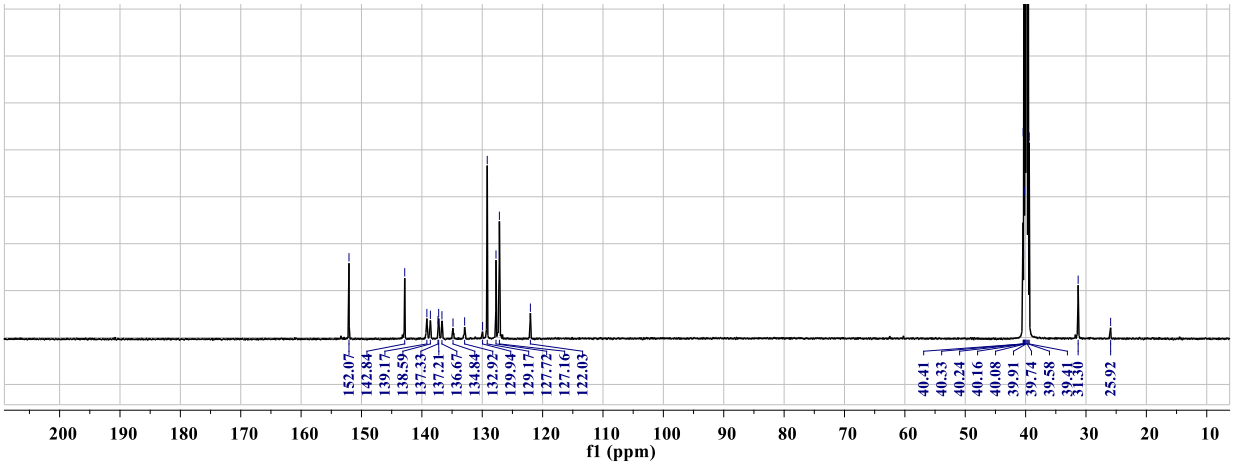
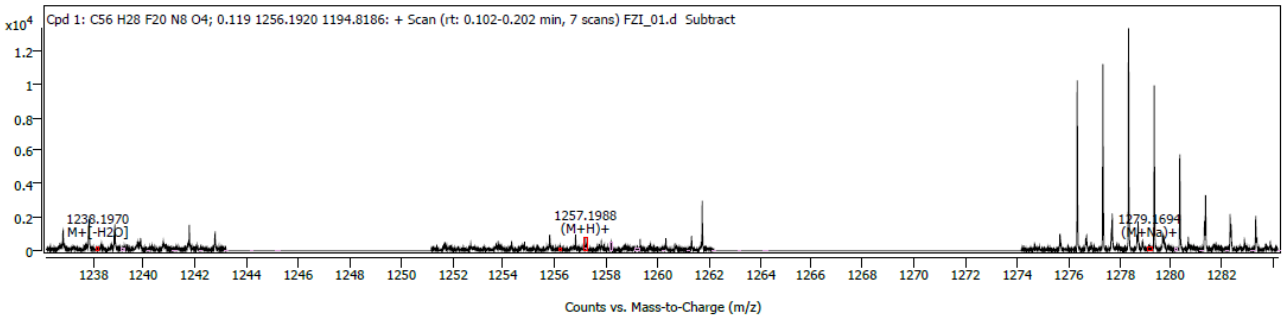


Figure S04 ^{13}C NMR spectrum of R in DMSO-d^{6}.



Spectrum Peaks

m/z	m/z (Calc)	Diff (ppm)	Abund	Height %	Height % (Calc)	Ion Species	Z
1238.1970	1238.1803	13.47	259	100.00	100.00	M+[-H2O]	1
1256.1855	1256.1909	-4.30	127	100.00	100.00	M+	1
1257.1988	1257.1987	0.06	808	100.00	100.00	(M+H)+	1
1279.1694	1279.1806	-8.81	251	100.00	100.00	(M+Na)+	1

Figure S05 ESI-HRMS of R.

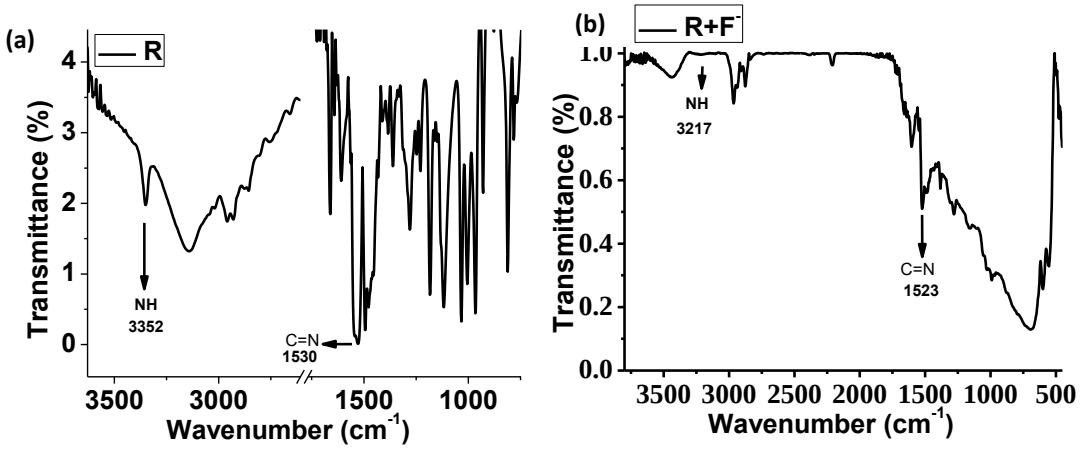


Figure S06 FTIR spectrum of (a) R and (b) R+F^- (KBr pellet).

S5 Visual detection:

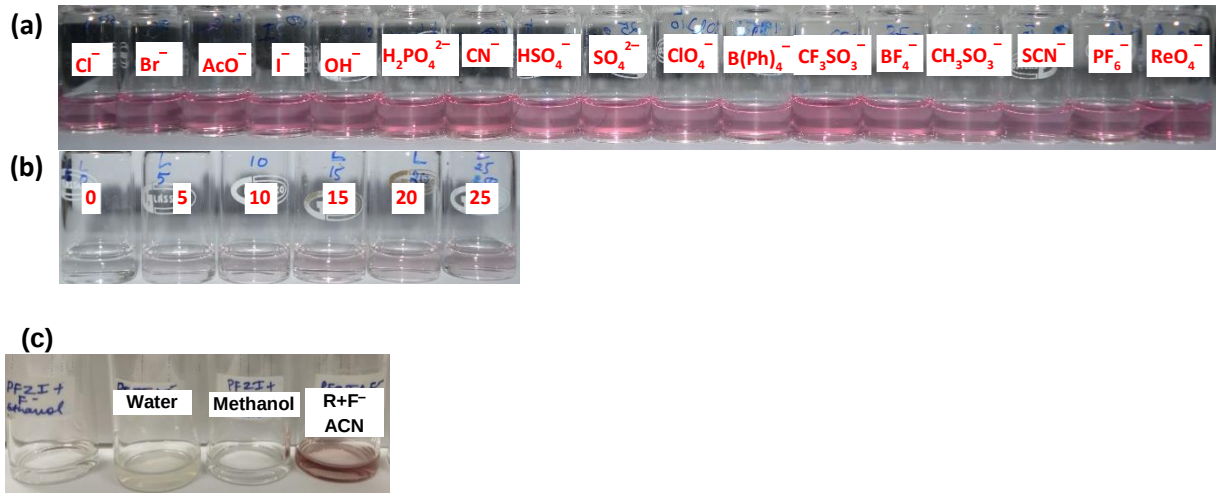


Figure S07 (a) Ion interference study (b) Visual detection of fluoride with variable concentration of the R (5 to 25 µL). (c) $R+F^-$ in different polar solvents.

S6 Synthesis and characterization of control molecule, S

4.09 mmol of 4-hydroxy benzaldehyde was dissolved in 20 mL methanol and 4.91 mmol of pentafluoro phenylhydrazine was added to the above solution, the color was changed from yellow to brown immediately. The reaction mixture was stirred at room temperature for 24 h to make sure completion of reaction. ^{1}H NMR ($CDCl_3$,) δ 7.78 (s, 1H, imine CH), δ 7.5 (d, 2H, Ph-CH), δ 6.85 (d, 2H, Ph-CH), δ 6.85 (s, 1H, Ph-OH) and δ 5.1 (s, 1H, NH).

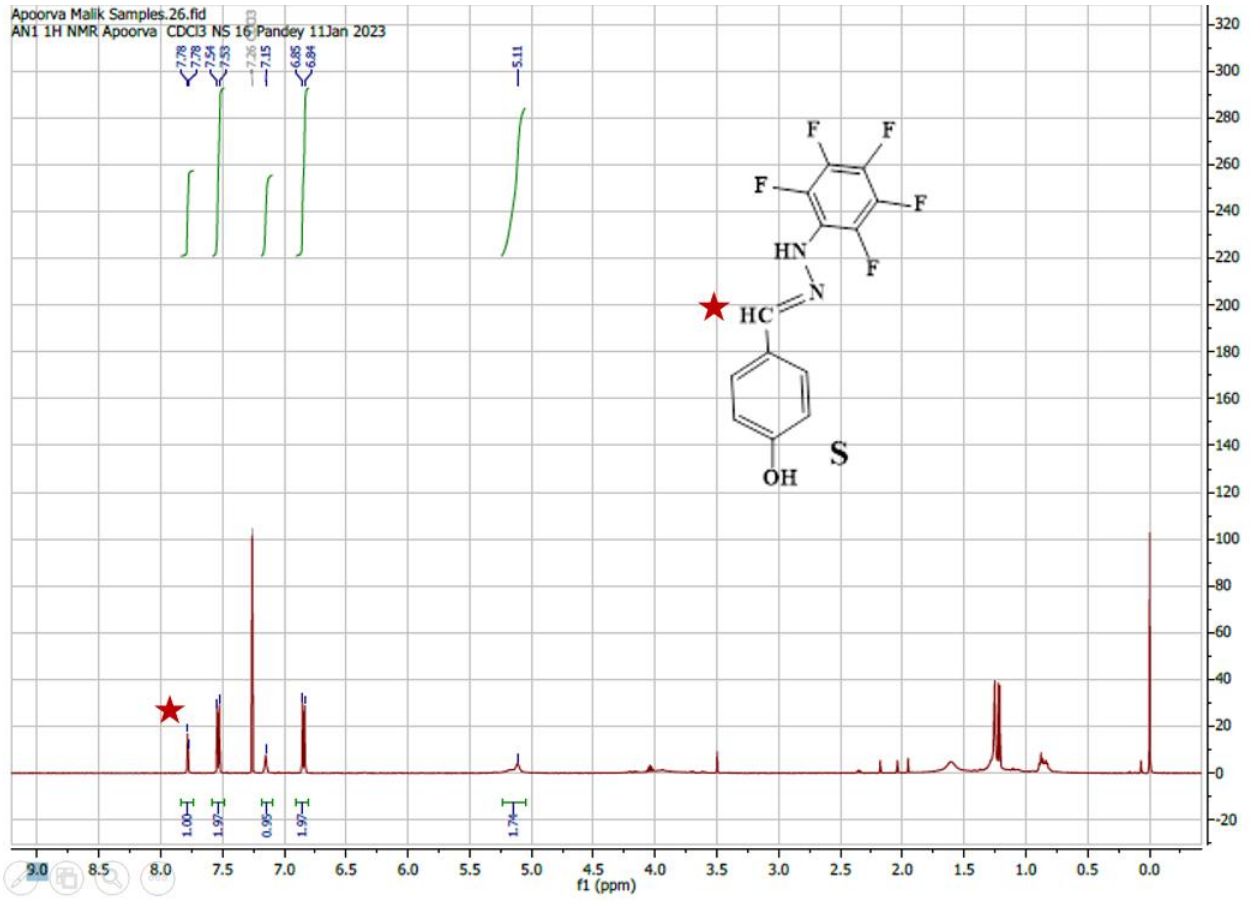


Figure S08 ^{1}H NMR spectrum of single armed molecule, S in $CDCl_3$.

S7 Visual experiment of S with fluoride

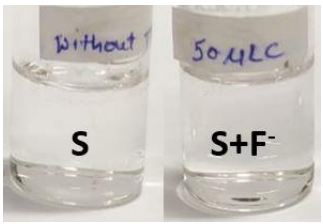


Figure S09 Control molecule, S and S + TBAF in acetonitrile.

S8 Absorption studies

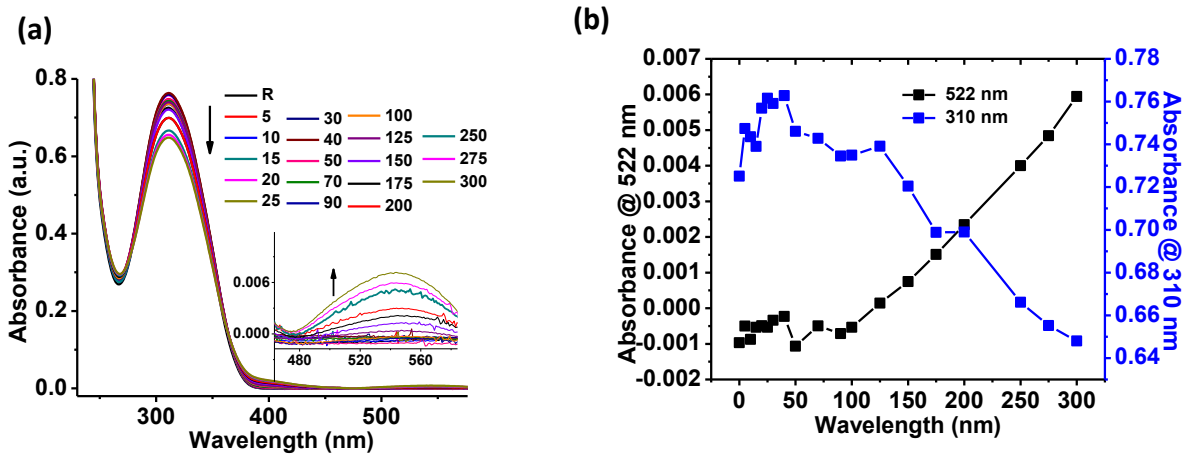


Figure S10 (a) Absorption spectra obtained from the titration of R with variable concentrations of fluoride in acetonitrile. (b) The data plotted for the band at 310 and 522 nm for the same titration.

S9 NMR data

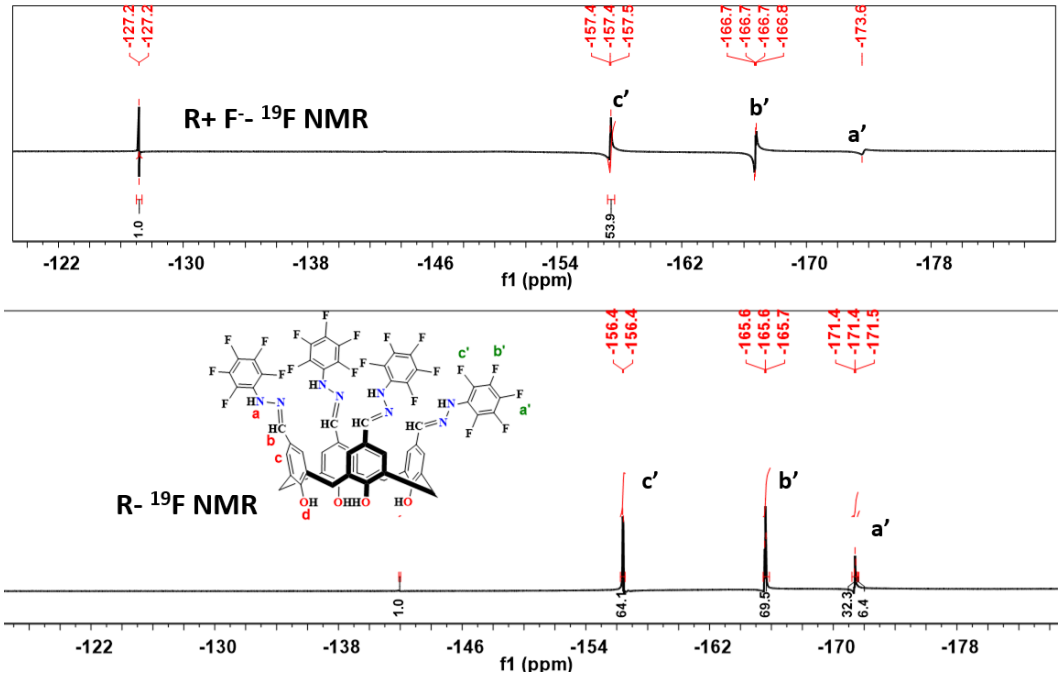


Figure S11 ^{19}F NMR spectrum of R and R+F^{-}.

S10 ESI MS of R+F^{-}:

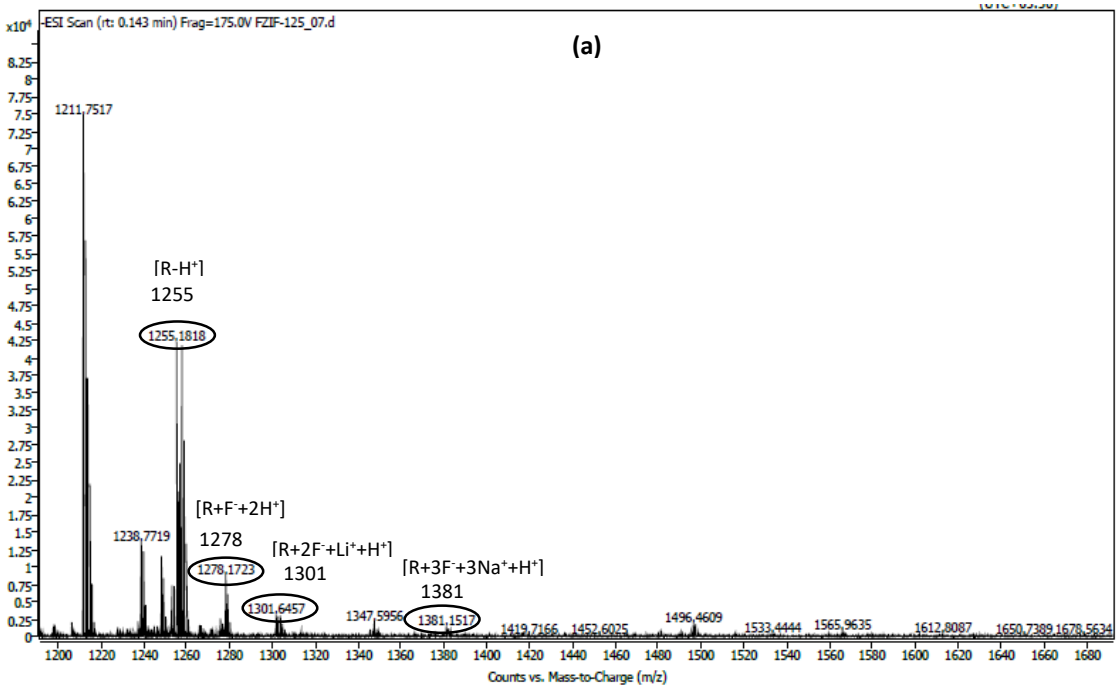


Figure S12 ESI spectrum of (a) R + 5 equv. F^-.

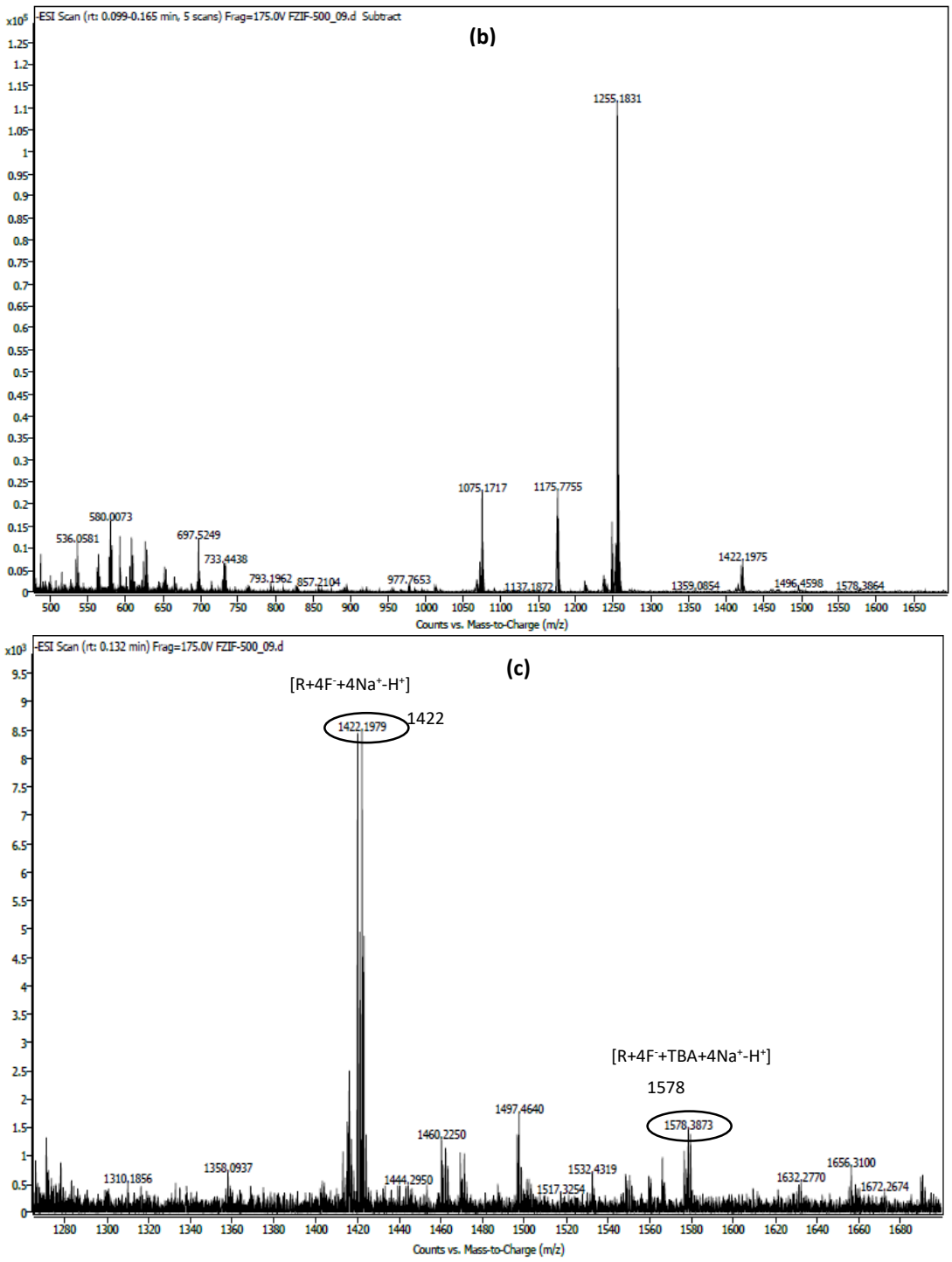
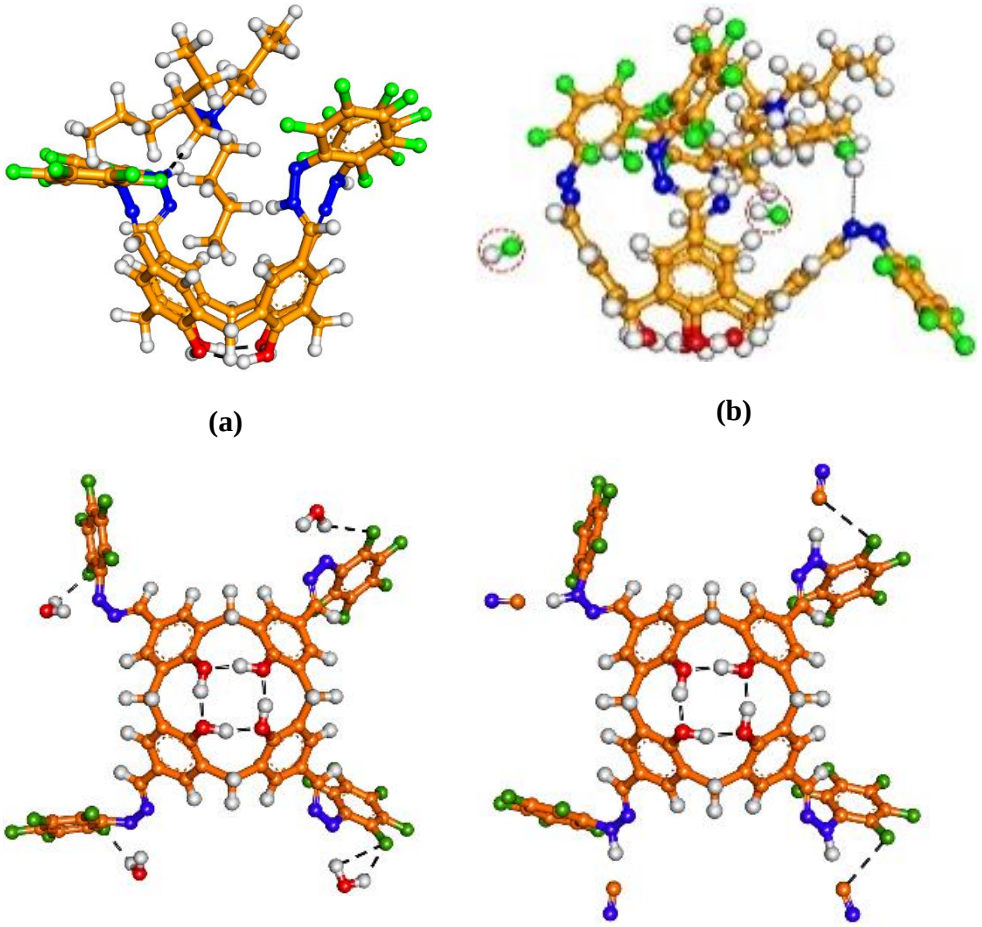


Figure S13 ESI spectrum of (b) R + 10 equv. F^- (c) same as (b) with zoomed area.

S11 Computational studies: DFT studies were extended to other two anions, OH^- and CN- that caused increase in the absorbance of R at 340 nm. In this case, $4CN^-$ and $4OH^-$ ions were placed at the vicinities of the binding arms of the -NH sites of the R.



(a) **(b)** **(c)** **(d)**

Figure S14 Final optimzed structures of (a) R+TBA (b) R +TBA+F^-. (c), (d) are the OH^- and CN^- ion addition to receptor (R).

S12 Gaussian reference:

Gaussian 09, Revision A.1, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, Jr., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.;

Rega, N.; Millam, N. J.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian, Inc., Wallingford CT, 2009.

S13 Structural coordinates:

5(a) : (Receptor **R)**

6	3.188611	-2.170699	2.747269
6	2.549650	-1.724546	3.907258
6	1.391876	-2.407559	4.334653
6	0.857910	-3.500513	3.621895
6	1.524966	-3.926007	2.469818
6	2.688751	-3.272462	2.032240
1	4.084003	-1.656937	2.399347
1	1.134597	-4.771666	1.897092
6	3.111550	1.415894	3.062576
6	2.497971	0.743209	4.121645
6	1.305237	1.281615	4.650089
6	0.713253	2.449527	4.129178
6	1.351705	3.097238	3.067242
6	2.549426	2.592756	2.536130
1	4.033929	1.017754	2.640825
1	0.915505	4.005298	2.644153
6	-3.149970	-3.358511	1.536742
6	-3.810434	-2.288476	2.167546
6	-3.391184	-1.825749	3.416889
6	-2.294259	-2.466824	4.029816
6	-1.607174	-3.531724	3.414153
6	-2.050184	-3.968475	2.162089
1	-4.652762	-1.801699	1.674930
1	-1.532436	-4.790878	1.660437
6	-2.379952	1.219329	4.344162
6	-3.445635	0.638993	3.627926
6	-3.896427	1.286361	2.473514
6	-3.299370	2.481721	2.041718
6	-2.229433	3.034567	2.768558
6	-1.752760	2.411201	3.923866
1	-4.719654	0.857035	1.897151
1	-1.753968	3.953273	2.423851
6	3.072906	-0.535525	4.668087
1	2.830483	-0.629731	5.753596
1	4.183027	-0.510626	4.633989
6	-0.412658	-4.168747	4.072509
1	-0.501601	-4.115578	5.183151
1	-0.381103	-5.257067	3.847028
6	-0.583279	2.975543	4.684117
1	-0.596191	4.086412	4.652221
1	-0.675044	2.726936	5.768031
6	-4.068049	-0.655604	4.077853
1	-5.157352	-0.659264	3.857389
1	-4.008004	-0.754731	5.187549
8	0.741334	-2.066832	5.503190
8	0.770554	0.623446	5.738375
8	-1.919691	0.673146	5.525616
8	-1.954946	-2.019300	5.291684
6	3.236545	3.260887	1.413523
1	3.906059	2.615855	0.826827
6	-3.763199	3.187457	0.831470
1	-3.443498	4.237024	0.754140
6	-3.640359	-3.803889	0.218145
1	-4.611603	-3.384932	-0.083000
6	3.402257	-3.705685	0.814428
1	3.978596	-2.919029	0.307515
7	-4.481870	2.538404	-0.042175
7	3.309643	-4.953188	0.447216
7	-2.908468	-4.623480	-0.484554
7	3.017112	4.530144	1.209957
7	-5.057948	3.113480	-1.135776
1	-5.190574	2.403965	-1.877806
7	-3.302037	-5.185278	-1.661582
7	3.824142	-5.450172	-0.712280
7	3.497820	5.227947	0.142743
1	3.581690	6.230937	0.385125
6	4.544759	4.744489	-0.723340
6	4.264868	3.749533	-1.684942
6	5.846984	5.290993	-0.725883

6	5.239846	3.312655	-2.595391
6	6.822493	4.880151	-1.644443
6	6.521804	3.880400	-2.581712
6	4.784520	-4.750311	-1.528522
6	6.133618	-5.154399	-1.635570
6	4.372535	-3.670637	-2.339598
6	7.029269	-4.526761	-2.511904
6	5.265479	-3.018406	-3.204175
6	6.597037	-3.447545	-3.297215
6	-4.701170	4.419498	-1.633298
6	-3.982361	4.609453	-2.834093
6	-5.154654	5.578565	-0.967158
6	-3.733936	5.886108	-3.356334
6	-4.892874	6.863581	-1.467634
6	-4.184980	7.022039	-2.667434
9	-3.528300	3.550565	-3.496908
9	-3.063354	6.021408	-4.494017
9	-3.944479	8.234532	-3.147601
9	-5.326854	7.931729	-0.808725
9	-5.853184	5.468346	0.155966
9	3.054337	3.209270	-1.747772
9	6.163518	6.226225	0.164152
9	8.032063	5.426698	-1.620261
9	7.442066	3.476588	-3.446784
9	4.943787	2.367047	-3.479296
9	6.573886	-6.162066	-0.888646
9	8.287099	-4.944105	-2.590108
9	3.112714	-3.255043	-2.301753
9	4.844936	-1.999517	-3.944565
9	7.440514	-2.839514	-4.120218
1	-2.471745	-5.426426	-2.231584
6	-4.430821	-4.726077	-2.431742
6	-4.290373	-4.056345	-3.667372
6	-5.744983	-5.024628	-2.010618
6	-5.397457	-3.708375	-4.453157
6	-6.863084	-4.661231	-2.777353
6	-6.693146	-4.005269	-4.004766
9	-5.221700	-3.088046	-5.613741
9	-7.747250	-3.668957	-4.735900
9	-3.074889	-3.746408	-4.107146
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9	-8.084830	-4.949940	-2.344494
1	4.015327	-6.462324	-0.609119
1	-2.178735	-0.320554	5.598580
1	-0.224525	0.858351	5.860861
1	0.973459	-1.107791	5.790201
1	-0.994892	-2.294760	5.534026

5(b) : (Receptor **R + 4F-)**

6	-2.328682	1.364634	3.862074
6	-1.686417	0.467424	4.723002
6	-0.338323	0.715452	5.038247
6	0.375975	1.814284	4.530663
6	-0.298227	2.695988	3.677914
6	-1.642070	2.473443	3.341125
1	-3.370805	1.191050	3.588469
1	0.224058	3.562529	3.264456
6	-2.983739	-2.065812	3.176267
6	-2.209948	-1.906724	4.315917
6	-1.181995	-2.835465	4.548633
6	-0.947350	-3.943164	3.717887
6	-1.720667	-4.076801	2.580266
6	-2.714358	-3.107545	2.235855
1	-3.785952	-1.365773	2.957101
1	-1.572961	-4.916570	1.900811
6	3.804809	1.246151	1.680630
6	4.253950	-0.058546	1.944086
6	3.938204	-0.690642	3.150994
6	3.169385	0.018783	4.091987
6	2.698068	1.324132	3.850634
6	3.030149	1.928491	2.635016
1	4.848646	-0.589898	1.199157
1	2.672988	2.939264	2.414505
6	2.257527	-3.482618	3.673677
6	3.409246	-3.085101	2.836874
6	3.529234	-3.562724	1.577535
6	2.560342	-4.502018	1.007252
6	1.514927	-5.010494	1.900451
6	1.347135	-4.519982	3.148711
1	4.368782	-3.261998	0.938585
1	0.835500	-5.771559	1.496873
6	-2.413328	-0.739110	5.248527
1	-2.082173	-0.984052	6.282394
1	-3.500662	-0.525499	5.356967
6	1.829766	2.029120	4.856757
1	2.062593	1.679071	5.889396
1	2.065884	3.116841	4.878013
6	0.175692	-4.910593	4.004657
1	-0.153674	-5.952407	3.794564
1	0.447594	-4.917251	5.083013
6	4.387585	-2.101998	3.419158
1	5.407265	-2.266840	3.004819
1	4.501861	-2.275120	4.515301
8	0.272977	-0.164257	5.955893
8	-0.348917	-2.638885	5.725446
8	2.063017	-2.954358	4.786434
8	2.858127	-0.521143	5.333086

6	-3.369195	-3.124147	0.979304
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6	2.546277	-4.862766	-0.300460
1	1.830937	-5.606516	-0.698245
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1	5.021711	1.410932	-0.125511
6	-2.351502	3.375365	2.409003
1	-3.014168	2.872434	1.689722
7	3.531092	-4.411645	-1.238373
7	-2.140293	4.656960	2.513778
7	3.425176	2.844092	-0.058296
7	-2.847838	-3.915462	-0.001932
7	3.429750	-3.655409	-2.185936
7	3.704324	3.553016	-1.183080
7	-2.623189	5.582072	1.642700
7	-3.207860	-4.029339	-1.194964
6	-4.287615	-3.342295	-1.849882
6	-4.259405	-1.962574	-2.146937
6	-5.366671	-4.083382	-2.379649
6	-5.241449	-1.351347	-2.939196
6	-6.354688	-3.486672	-3.176127
6	-6.295503	-2.114537	-3.459092
6	-3.656083	5.299854	0.672752
6	-4.984232	5.755389	0.815038
6	-3.333389	4.614086	-0.517185
6	-5.946418	5.554112	-0.183790
6	-4.291995	4.390067	-1.518518
6	-5.602008	4.863648	-1.356258
6	2.240862	-2.947955	-2.619323
6	1.653094	-1.909114	-1.871800
6	1.709709	-3.225252	-3.893807
6	0.580232	-1.160661	-2.374464
6	0.625940	-2.492170	-4.403928
6	0.057838	-1.458035	-3.644479
9	2.139931	-1.619829	-0.670383
9	0.058941	-0.177374	-1.651486
9	-0.958176	-0.759429	-4.126362
9	0.141082	-2.778181	-5.606368
9	2.230662	-4.201361	-4.623756
9	-3.269663	-1.210233	-1.673209
9	-5.462050	-5.383066	-2.120072
9	-7.353619	-4.217832	-3.659920
9	-7.230432	-1.543380	-4.210550
9	-5.176386	-0.048682	-3.196566
9	-5.336988	6.398755	1.923260
9	-7.183126	6.007327	-0.017629
9	-2.098112	4.169981	-0.710133
9	-3.954591	3.738079	-2.624279
9	-6.508120	4.662919	-2.302380
6	4.645418	3.114258	-2.186508
6	4.243895	2.600626	-3.438601
6	6.030932	3.266116	-1.966800
6	5.172399	2.265661	-4.433743
6	6.972220	2.916222	-2.947908
6	6.545334	2.418641	-4.187375
9	4.755101	1.794063	-5.602448
9	7.431154	2.094890	-5.119126
9	2.949978	2.429993	-3.688568
9	6.469274	3.753587	-0.813187
9	8.269054	3.065732	-2.704836
1	2.994732	-1.535476	5.336152
1	0.615639	-3.070646	5.494147
1	-0.051856	-1.519604	5.706207
1	1.313262	-0.139924	5.830443
1	5.738465	-2.634256	-2.019893
9	5.932494	-1.977060	-1.334704
1	-1.304027	-4.654073	-1.871441
9	-0.345193	-4.701678	-2.065205
1	-2.723145	6.500648	2.109250
9	0.675294	5.827458	0.978559
1	2.839384	3.972790	-1.568584
9	2.088660	5.960522	0.822534

S11(a) : (R+ TBA)

6	1.874476	0.641199	4.205621
6	1.074042	-0.022544	5.140037
6	1.281737	-1.403871	5.335397
6	2.280748	-2.119114	4.639189
6	3.067835	-1.426497	3.716081
6	2.847872	-0.061173	3.481883
1	1.734551	1.708874	4.035493
1	3.843823	-1.955473	3.159278
6	-1.402136	1.913837	4.125936
6	-1.227866	0.820017	4.973718
6	-2.191273	-0.214861	4.941864
6	-3.288552	-0.188304	4.055858
6	-3.416053	0.907757	3.194755
6	-2.489294	1.958521	3.236561
1	-0.684957	2.734610	4.150540
1	-4.247339	0.948578	2.488954
6	1.615420	-5.239346	1.483098
6	0.265407	-5.588147	1.656387
6	-0.389572	-5.312032	2.858456
6	0.346075	-4.692543	3.892901
6	1.697054	-4.326246	3.735677
6	2.322472	-4.609112	2.516561
1	-0.282382	-6.064107	0.842129

1	3.368091	-4.334024	2.364914
6	-3.126547	-3.483279	3.469440
6	-2.703387	-4.484878	2.573139
6	-3.093890	-4.379820	1.234240
6	-3.895158	-3.310654	0.806916
6	-4.287967	-2.312112	1.713946
6	-3.901728	-2.378722	3.054839
1	-2.776420	-5.137199	0.514873
1	-4.896601	-1.475332	1.370868
6	-0.022543	0.708248	5.866415
1	-0.292821	0.182390	6.813966
1	0.326270	1.710076	6.197975
6	2.437749	-3.602934	4.827656
1	2.067651	-3.912819	5.833851
1	3.512681	-3.887955	4.832937
6	-4.294950	-1.306439	4.033771
1	-5.307096	-0.912893	3.793137
1	-4.410981	-1.746425	5.054226
6	-1.847870	-5.631643	3.039893
1	-2.116224	-6.563819	2.495973
1	-2.058565	-5.869362	4.110627
8	0.528648	-2.136532	6.224959
1	-0.324282	-1.636170	6.486224
8	-2.001953	-1.225831	5.848757
8	-2.845244	-3.550348	4.817910
8	-0.330082	-4.495001	5.077533
1	0.156166	-3.830594	5.683040
1	-2.079731	-4.205737	5.007413
1	-2.585829	-2.046129	5.635822
6	-2.643617	3.151134	2.376642
1	-2.564469	4.110551	2.913588
6	-4.371652	-3.232437	-0.590685
1	-5.427440	-2.944045	-0.699703
6	2.275472	-5.549268	0.196775
1	2.063421	-6.550384	-0.208326
6	3.606794	0.629033	2.424720
1	4.592385	1.027535	2.679664
7	-3.538340	-3.519618	-1.549118
7	3.058966	0.735675	1.225845
1	2.102898	0.308498	1.077908
7	3.031622	-4.632125	-0.339537
7	-2.858960	2.989699	1.103761
7	-3.834730	-3.394806	-2.878021
1	-3.233780	-4.037837	-3.426343
7	3.596316	-4.874866	-1.580528
1	3.869745	-5.844655	-1.808980
7	3.470930	1.336899	0.119753
7	-2.915850	4.031179	0.204904
1	-3.605405	3.788632	-0.536580
6	-3.037536	5.409263	0.640015
6	-1.896374	6.099094	1.097972
6	-4.239899	6.142501	0.553992
6	-1.947888	7.456067	1.452190
6	-4.304542	7.502689	0.888158
6	-3.153653	8.165124	1.344276
6	4.805810	1.787537	-0.017472
6	5.950565	0.961171	0.107497
6	5.033759	3.108308	-0.469981
6	7.237510	1.417382	-0.203797
6	6.313800	3.572248	-0.804148
6	7.425237	2.728657	-0.667480
6	4.554793	-3.880459	-1.966104
6	5.871763	-4.220679	-2.359628
6	4.188893	-2.518993	-2.074765
6	6.771645	-3.266035	-2.850549
6	5.090106	-1.554298	-2.549661
6	6.384278	-1.920424	-2.941689
6	-5.192808	-3.326193	-3.371232
6	-5.903900	-2.110720	-3.305730
6	-5.835684	-4.412715	-4.003406
6	-7.195311	-1.982381	-3.840131
6	-7.117856	-4.295008	-4.558052
6	-7.806448	-3.074444	-4.472901
9	-5.349226	-1.049465	-2.730582
9	-7.834014	-0.821349	-3.752897
9	-9.022100	-2.955158	-4.985815
9	-7.683465	-5.337029	-5.153161
9	-5.210415	-5.582338	-4.081848
9	-0.735235	5.461217	1.202363
9	-5.345661	5.533047	0.139720
9	-5.452099	8.159225	0.782263
9	-3.205753	9.447747	1.669928
9	-0.852259	8.068906	1.882826
9	5.807270	-0.295866	0.519887
9	8.278734	0.606022	-0.069354
9	4.007630	3.946577	-0.586999
9	6.473197	4.816271	-1.239361
9	8.639687	3.164559	-0.973108
9	2.966527	-2.117444	-1.742007
9	4.705695	-0.285318	-2.641450
9	7.230789	-1.005592	-3.395321
9	7.992362	-3.632221	-3.217175
9	6.277433	-5.484183	-2.266073
7	0.384211	2.069558	-2.499013
6	1.599810	2.226706	-3.435451
1	1.512558	3.201763	-3.970926
1	2.517817	2.303725	-2.799100
6	1.770411	1.090855	-4.448069

1	0.851880	0.931376	-5.045674
1	1.974384	0.127514	-3.936935
6	2.936345	1.408707	-5.401225
1	3.869760	1.572369	-4.824578
1	2.743187	2.357156	-5.941689
6	3.149202	0.282107	-6.406206
1	2.268619	0.116940	-7.037849
1	3.986631	0.510861	-7.080351
1	3.388395	-0.669171	-5.915941
6	-0.885797	1.960560	-3.354015
1	-0.909445	0.944022	-3.814095
1	-0.803812	2.687009	-4.198174
6	-2.195401	2.214318	-2.603387
1	-2.226706	3.249509	-2.208082
1	-2.283060	1.544159	-1.714174
6	-3.398637	1.988335	-3.531348
1	-3.447521	0.923571	-3.838545
1	-3.281960	2.569036	-4.468527
6	-4.703559	2.384805	-2.847841
1	-4.764467	3.463177	-2.665305
1	-5.568260	2.123767	-3.475466
1	-4.843268	1.866642	-1.891459
6	0.602257	0.790302	-1.674615
1	1.672487	0.784409	-1.335202
1	0.492105	-0.087477	-2.354271
6	-0.319285	0.616099	-0.465844
1	-1.392830	0.617154	-0.773749
1	-0.226365	1.460364	0.247410
6	0.001896	-0.704840	0.251420
1	-0.199594	-1.565949	-0.421256
1	1.088070	-0.763855	0.487941
6	-0.808669	-0.861607	1.530730
1	-1.890459	-0.866533	1.334657
1	-0.580196	-1.814741	2.028410
1	-0.618359	-0.060572	2.255288
6	0.348078	3.288957	-1.564980
1	1.291565	3.291424	-0.965422
1	-0.476305	3.144425	-0.821109
6	0.151593	4.630499	-2.279263
1	-0.620926	5.211638	-1.726726
1	-0.276263	4.505707	-3.293285
6	1.435841	5.468900	-2.355789
1	2.255329	4.894164	-2.828877
1	1.790680	5.709026	-1.331544
6	1.207758	6.764084	-3.128088
1	2.125907	7.367429	-3.162778
1	0.904645	6.584460	-4.165496
1	0.437247	7.391248	-2.663248

S11(b): (R +TBA+F^-)

6	-0.734856	-0.535526	4.064426
6	-1.591795	-1.609908	4.316646
6	-1.048769	-2.904116	4.348545
6	0.320993	-3.150258	4.148979
6	1.152893	-2.058713	3.898063
6	0.638377	-0.744127	3.833811
1	-1.125003	0.481500	4.061701
1	2.218506	-2.217073	3.740322
6	-3.954701	0.139080	2.759463
6	-3.737425	-1.117990	3.208804
6	-4.097152	-2.275840	2.371368
6	-4.663410	-2.025242	1.029882
6	-4.869676	-0.754897	0.611251
6	-4.557798	0.402847	1.450012
1	-3.672253	1.008840	3.366532
1	-5.268140	-0.558776	-0.390760
6	2.175249	-5.524204	0.724220
6	1.052865	-6.175946	0.167161
6	-0.138304	-6.265499	0.880656
6	-0.185018	-5.729427	2.190607
6	0.946437	-5.119063	2.788024
6	2.115247	-5.010810	2.036426
1	1.099470	-6.576159	-0.851590
1	2.989570	-4.524975	2.475282
6	-3.130200	-4.923601	0.118255
6	-2.027341	-5.578569	-0.452823
6	-1.466759	-5.023079	-1.588173
6	-1.942953	-3.790625	-2.130335
6	-3.144138	-3.242112	-1.583078
6	-3.736494	-3.795722	-0.457051
1	-0.619017	-5.502390	-2.080360
1	-3.573739	-2.362012	-2.054345
6	-3.067038	-1.387871	4.526874
1	-3.535897	-2.267904	5.027692
1	-3.224969	-0.547531	5.240091
6	0.867712	-4.553202	4.179030
1	0.239562	-5.201848	4.835323
1	1.865896	-4.565075	4.670761
6	-4.982068	-3.203291	0.154128
1	-5.685647	-2.914770	-0.662201
1	-5.549493	-3.972198	0.727815
6	-1.387430	-6.770714	0.214861
1	-1.164476	-7.562932	-0.534277
1	-2.066311	-7.267285	0.941600
8	-1.850089	-4.023456	4.629792
1	-2.816785	-3.814171	4.414609

8	-3.923290	-3.435202	2.819181
8	-3.676862	-5.470064	1.356158
8	-1.377933	-5.843667	2.841054
1	-1.412531	-5.259497	3.733396
1	-2.821920	-5.690019	1.965913
1	-4.073213	-4.566988	1.948976
6	-4.771351	1.686807	1.064097
1	-4.484871	2.544116	1.704371
6	-1.207383	-3.093687	-3.125891
1	-1.677303	-2.268412	-3.652314
6	3.336963	-5.381402	-0.138749
1	3.438508	-6.080067	-1.012723
6	1.559561	0.345203	3.543395
1	2.568342	0.216186	3.942580
7	0.081351	-3.483447	-3.331978
7	1.169190	1.406246	2.842483
7	4.225830	-4.456224	-0.028549
7	-5.181682	2.083995	-0.241868
7	0.961683	-2.973771	-4.065199
7	5.205969	-3.809215	0.255986
7	1.887015	2.435701	2.533960
7	-6.264031	2.216638	-0.774388
6	-7.574015	1.962545	-0.210577
6	-8.099929	2.688090	0.876117
6	-8.430555	1.063900	-0.877041
6	-9.432650	2.536204	1.283407
6	-9.763394	0.891923	-0.471664
6	-10.270510	1.634139	0.606689
6	3.268686	2.577602	2.812969
6	4.285852	1.706283	2.347668
6	3.726465	3.756741	3.459497
6	5.649335	1.978768	2.513341
6	5.084966	4.049857	3.618249
6	6.060896	3.157422	3.146164
6	5.484004	-2.493453	-0.215162
6	6.852790	-2.114204	-0.155178
6	4.551100	-1.535779	-0.689343
6	7.269032	-0.843382	-0.572855
6	4.966206	-0.263228	-1.098704
6	6.327855	0.086254	-1.046494
6	0.812049	-1.898187	-5.002461
6	1.698965	-0.801693	-4.925183
6	-0.073712	-1.915300	-6.103257
6	1.701288	0.224934	-5.878998
6	-0.083028	-0.895921	-7.066327
6	0.804891	0.183800	-6.955644
9	2.565580	-0.725916	-3.917547
9	2.547896	1.243332	-5.758043
9	0.797135	1.156928	-7.858954
9	-0.934696	-0.948760	-8.083913
9	-0.918394	-2.930495	-6.251307
9	-7.317733	3.542477	1.524813
9	-7.966698	0.347170	-1.891286
9	-10.543737	0.029907	-1.111343
9	-11.528708	1.481847	0.986976
9	-9.898749	3.239427	2.307515
9	3.951186	0.585021	1.707751
9	6.555552	1.117968	2.057361
9	2.837293	4.617864	3.948506
9	5.457451	5.171418	4.223846
9	7.352309	3.426691	3.298978
9	3.265798	-1.841962	-0.721078
9	4.076066	0.620026	-1.534997
9	6.718758	1.284241	-1.440708
9	8.555246	-0.517872	-0.517790
9	7.754757	-2.973934	0.284385
7	1.184615	4.624259	-0.429965
6	2.526782	5.038096	0.202112
1	2.413244	6.059890	0.651020
1	2.717047	4.354640	1.069147
6	3.718630	5.011694	-0.756737
1	3.643015	5.819837	-1.511489
1	3.755529	4.060991	-1.327461
6	5.031237	5.179513	0.027631
1	5.170309	4.327174	0.723736
1	4.985306	6.086069	0.665034
6	6.228899	5.277503	-0.910790
1	6.172961	6.159272	-1.560427
1	7.166035	5.360033	-0.342873
1	6.322376	4.398011	-1.557525
6	0.953084	5.488999	-1.673132
1	1.709040	5.202655	-2.442002
1	1.168305	6.549592	-1.394462
6	-0.441884	5.409251	-2.299933
1	-1.242545	5.538718	-1.546342
1	-0.612979	4.403075	-2.748782
6	-0.589415	6.481756	-3.391957
1	0.208576	6.366281	-4.153197
1	-0.454485	7.492793	-2.958418
6	-1.952868	6.394889	-4.069422
1	-2.776378	6.533380	-3.358954
1	-2.059341	7.166159	-4.843312
1	-2.106798	5.425304	-4.559607
6	1.289675	3.129565	-0.780171
1	1.607961	2.588055	0.154934
1	2.112710	2.998296	-1.518061
6	0.004651	2.490654	-1.309262
1	-0.223494	2.848928	-2.338236

1	-0.871701	2.781780	-0.689712
6	0.134644	0.959525	-1.308478
1	0.990040	0.647260	-1.939224
1	0.361289	0.597944	-0.283491
6	-1.141946	0.295441	-1.813461
1	-1.382989	0.598221	-2.838701
1	-1.034051	-0.800564	-1.819708
1	-2.003268	0.535729	-1.181778
6	0.087624	4.802220	0.631418
1	0.405630	4.234404	1.551005
1	-0.829883	4.276495	0.265177
6	-0.255934	6.248471	0.990133
1	-1.330327	6.279665	1.281256
1	-0.188887	6.922804	0.113772
6	0.580315	6.812670	2.147202
1	1.660713	6.802274	1.880764
1	0.485629	6.158074	3.039009
6	0.155091	8.232239	2.504677
1	0.759037	8.626502	3.333368
1	0.270618	8.925669	1.664157
1	-0.892339	8.278158	2.827032
1	2.646925	-3.754589	-3.457515
9	3.389339	-4.079014	-2.893383
1	-4.200505	3.012479	-2.423479
9	-3.384004	3.532475	-2.434457
1	5.741290	-7.544944	2.247186
9	5.160159	-6.936782	1.767440
1	-0.561112	1.775429	2.214318
9	-1.473079	2.039894	1.933347