Supporting Information

A "turn on" fluorescent and chromogenic chemosensor for fluoride anion: Experimental and DFT study.

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1. Determination the binding constant

For 1:2 binding constant: The binding of two guests (F^-) to single host molecule (BTA) gives two binding constants (K_1 and K_2). These values we have obtained by fitting the equation 12 into Origin software program according to literature reported method[1].

For 1:2 binding, we have two equilibrium equations (Eqn (1),(2)), two binding constant expression (eqn (3), (4)) and two mass balance equation (eqn (5), (6)).

$$BTA + F^- \rightleftharpoons BTA.F \quad (1)$$

$$BTA.F + F^- \rightleftharpoons BTA.2F \quad (2)$$

$$K_1 = [BTA.F]/([BTA][F^-]) \quad (3)$$

$$K_2 = [BTA.2F]/([BTA.F][F^-]) \quad (4)$$

$$[BTA]_t = [BTA] + [BTA.F] + [BTA.2F] \quad (5)$$

$$[F^-]_t = [F^-] + [BTA.F] + 2[BTA.2F] \quad (6)$$

Equation (3)-(5) are combined to give equation (7)-(9)

$$[BTA] = \frac{[BTA]_t}{1 + K_1[F^-] + K_1K_2[F^-]^2} \quad (7)$$

$$[BTA.F] = \frac{K_1[F^-][BTA]_t}{1 + K_1[F^-] + K_1K_2[F^-]^2} \quad (8)$$

$$[BTA.2F] = \frac{K_1\,K_2[F^-]^2[BTA]_t}{1 + K_1[F^-] + K_1K_2[F^-]^2} \quad (9)$$

According to Beers lamberts law, we have obtained equation 10.

$$A = \varepsilon_{BTA}\, b[BTA] + \varepsilon_{F^-}\, b[F^-] + \varepsilon_{BTA.F}\, b[BTA.F] + \varepsilon_{BTA.2F}\, b[BTA.2F] \quad (10)$$

The receptor BTA has an absorbance at 385 nm and the F^- anion is transparent at this wavelength. The UV-visible titration is performed by keeping the $[BTA]_t$ constant with an incremental addition of $[F^-]$. As a result, equation 10 can be simplified to equation 11. By substituting the equation (7)-(9) into the equation 11; equation 12 is obtained in which absorbance is dependent on the anion concentration.

$$A = \varepsilon_{BTA}\, b[BTA] + \varepsilon_{BTA.F}\, b[BTA.F] + \varepsilon_{BTA.2F}\, b[BTA.2F] \quad (11)$$

$$A = \frac{\varepsilon_{BTA}\, b + \varepsilon_{BTA.F} b K_1 [F^-] + \varepsilon_{BTA.2F}\, b\, K_1 K_2 [F^-]^2}{1 + K_1[F^-] + K_1 K_2 [F^-]^2} [BTA]_t \quad (12)$$

By fitting this equation by iterative data fitting procedure in the origin software, we have obtained K_1 and K_2 48.36 M^{-1} and 1.578× 10^7 M^{-1} respectively.

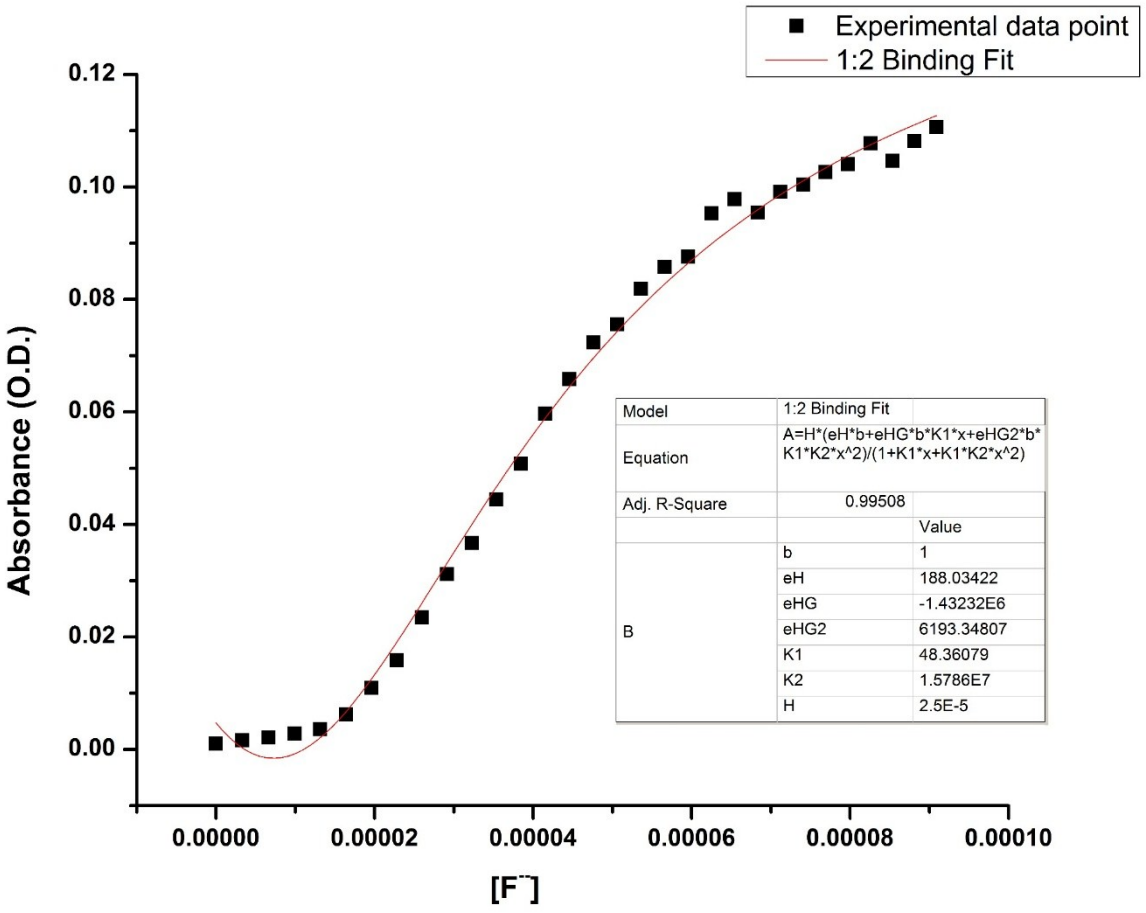

Figure S1: Graph of absorbance at 488nm v/s fluoride anion concentration obtained by iterative data fitting procedure in the origin software.

2. Calculation of detection limit

The detection limit was calculated based on the UV-spectrophotometric titration data. A good linear relationship between the absorbance (ΔA) and the [F^-] concentration could be

obtained. The absorbance of BTA without anion [F^-] was measured 10 times and the standard deviation of blank measurements was determined. The detection limit was calculated by using this equation ($3\sigma/S$), where σ = standard deviation of BTA absorbance, S= slope between the absorbance versus [F^-] concentration. The limit of detection for [F^-] was 4.1×10^{-7} M.

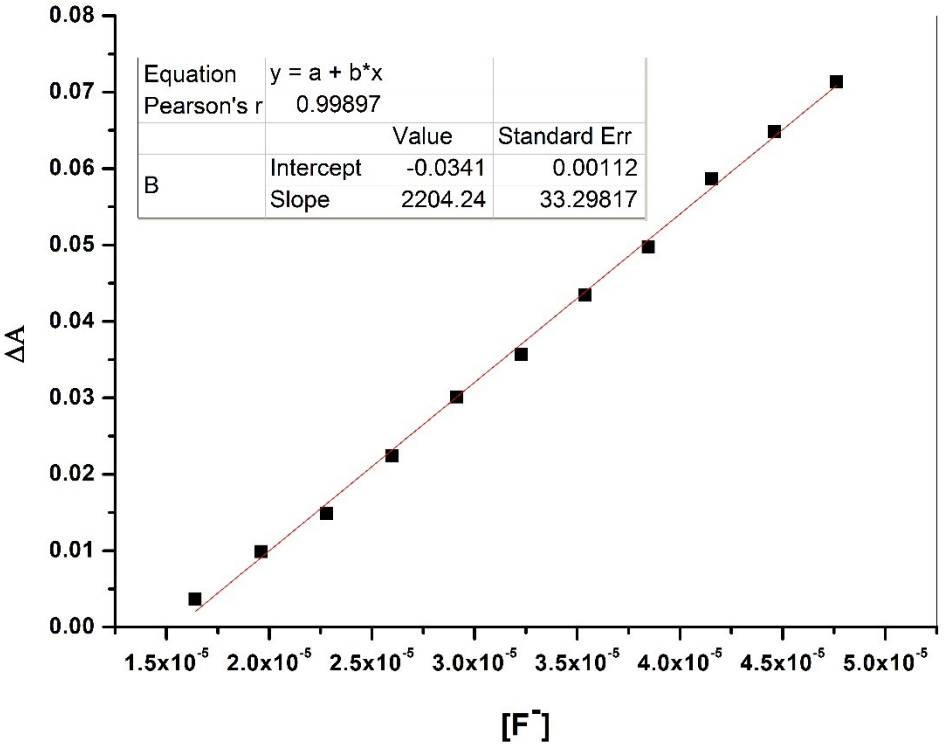

Figure S2: Absorbance at 488 nm for BTA (25 µM in acetonitrile) as a function of the concentration of F^- ion. The lowest detection limit is 4.1×10^{-7} M.

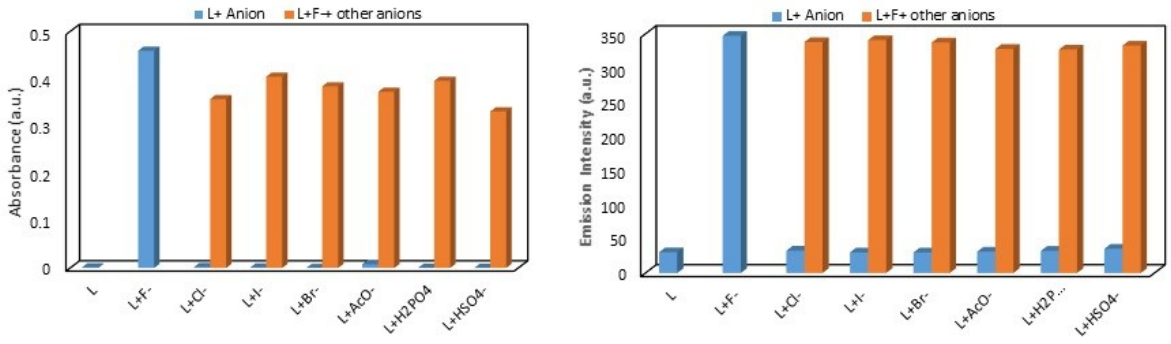

Figure S3: Interference plots of **BTA** with F^- ion in the presence of other anions. Competitive binding experiments.

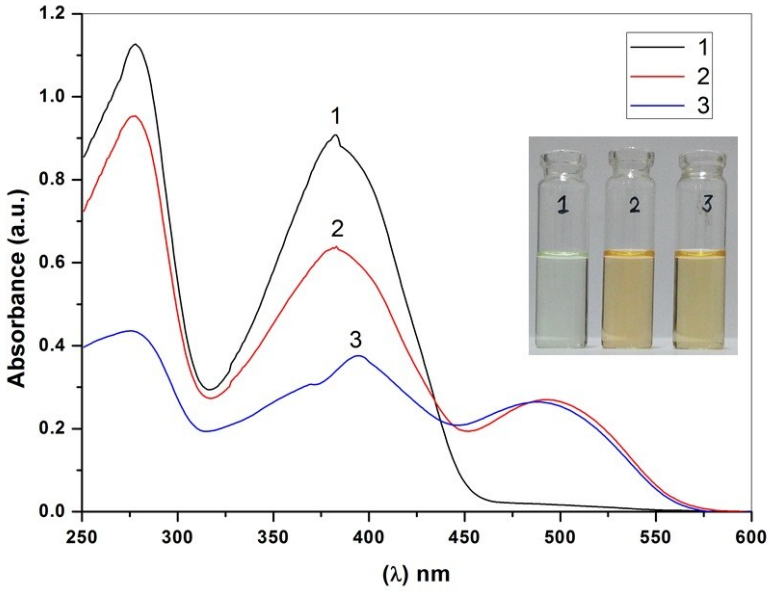

Figure S4: Absorption spectra of (1) L (BTA) in acetonitrile (2) L+F^- in acetonitrile (3) L+F^- in acetonitrile containing 5% water.

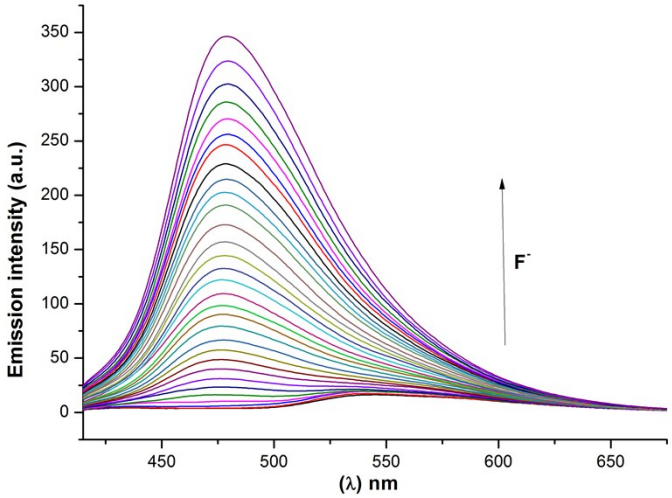

Figure S5: Emission titration plot of receptor BTA (25 µM) with increasing F^- (1mM) ion concentration (0 to 300 µL) in acetonitrile (λ_{ex} = 385 nm).

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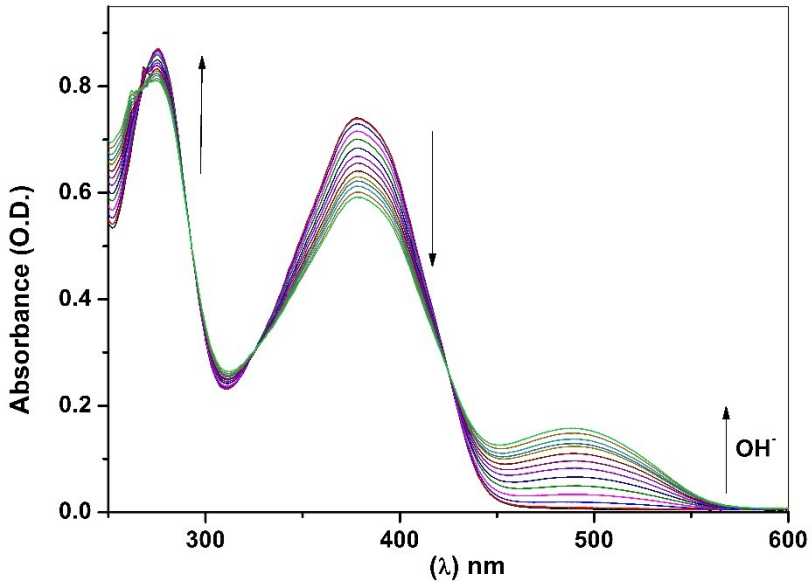
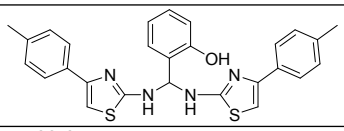
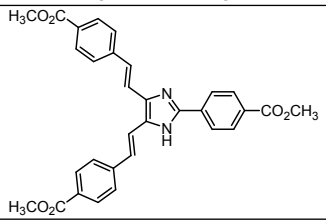
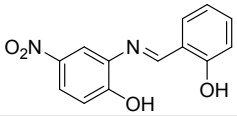
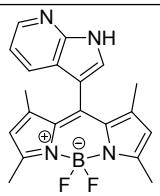
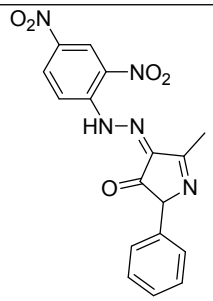
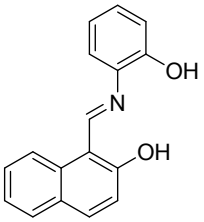


Figure S6: Changes in absorption spectra of L (25µM) upon addition of TBAOH (1mM) in acetonitrile.

Table S1: Data of comparison with other reported receptors.

Sr. No.	Receptors	Anion detected	Binding constant (M^{-1})	Detection limit (M)	Reference
1		F^-	5.4×10^4	4.1×10^{-7}	This work
2		F^- AcO^-	7.3×10^3 3.5×10^3	NA NA	[2]
3		F^- AcO^- $H_2PO_4^-$	2.0×10^4 2.2×10^4 9.6×10^3	1.2×10^{-6} 1.23×10^{-6} 3.20×10^{-6}	[3]
4		F^- AcO^-	3.43×10^4 NA	1.21×10^{-6} NA	[4]

5		F^- AcO^- $H_2PO_4^-$	5.40×10^4 4.73×10^3 2.57×10^3	NA NA NA	[5]
6		F^- AcO^- $H_2PO_4^-$	7.76×10^4 6.24×10^3 NA	NA NA NA	[6]

Note N.A.= Not available

Natural bond orbital analysis (NBO):

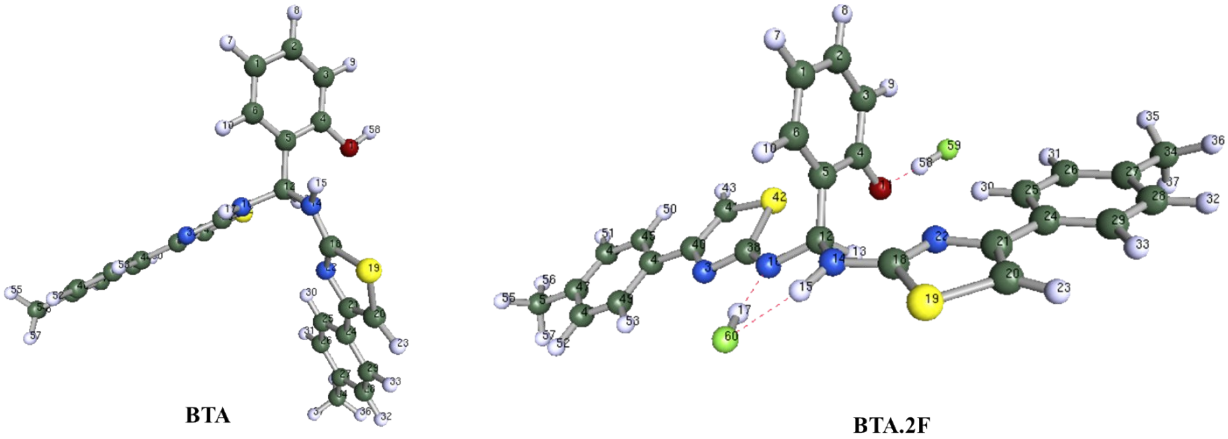


Figure S7: Geometry optimised structure of BTA, BTA.$2F^-$.

Table S2: Summary of Natural population analysis of BTA.

No	Atom	Natural charge	Natural population			
			Core	Valence	Rydberg	Total
1	c	-0.2495	1.99894	4.23396	0.01659	6.2495
2	c	-0.20148	1.99896	4.18649	0.01603	6.20148
3	c	-0.29416	1.9989	4.27859	0.01667	6.29416
4	c	0.35999	1.99857	3.61763	0.0238	5.64001
5	c	-0.13489	1.99878	4.11732	0.01879	6.13489
6	c	-0.19739	1.99891	4.18221	0.01628	6.19739
7	h	0.22955	0	0.76884	0.00161	0.77045
8	h	0.23108	0	0.76725	0.00168	0.76892
9	h	0.23371	0	0.76451	0.00178	0.76629
10	h	0.23108	0	0.76653	0.00239	0.76892
11	o	-0.69271	1.9997	6.68303	0.00998	8.69271

12	c	0.16535	1.99901	3.80299	0.03265	5.83465
13	h	0.24706	0	0.74707	0.00587	0.75294
14	n	-0.64779	1.9991	5.63367	0.01502	7.64779
15	h	0.42426	0	0.57294	0.0028	0.57574
16	n	-0.652	1.9991	5.63692	0.01597	7.652
17	h	0.42562	0	0.57016	0.00422	0.57438
18	c	0.3384	1.99912	3.62524	0.03725	5.6616
19	s	0.32675	9.99888	5.63724	0.03713	15.67325
20	c	-0.4248	1.99894	4.40863	0.01723	6.4248
21	c	0.13976	1.99885	3.8344	0.02699	5.86024
22	n	-0.60258	1.99917	5.58611	0.01729	7.60258
23	h	0.25577	0	0.74328	0.00096	0.74423
24	c	-0.09178	1.99884	4.0762	0.01674	6.09178
25	c	-0.19607	1.99894	4.18066	0.01648	6.19607
26	c	-0.21701	1.99889	4.20217	0.01595	6.21701
27	c	-0.04342	1.99886	4.02923	0.01533	6.04342
28	c	-0.21808	1.99889	4.20311	0.01607	6.21808
29	c	-0.19444	1.99894	4.18009	0.01541	6.19444
30	h	0.23308	0	0.76338	0.00355	0.76692
31	h	0.22393	0	0.77426	0.00181	0.77607
32	h	0.22502	0	0.7732	0.00177	0.77498
33	h	0.22363	0	0.77442	0.00195	0.77637
34	c	-0.61589	1.99924	4.60687	0.00978	6.61589
35	h	0.22072	0	0.77787	0.00141	0.77928
36	h	0.2185	0	0.78013	0.00137	0.7815
37	h	0.22576	0	0.77274	0.0015	0.77424
38	c	0.34257	1.99913	3.62028	0.03802	5.65743
39	n	-0.60999	1.99918	5.59257	0.01823	7.60999
40	c	0.14048	1.99885	3.83326	0.02741	5.85952
41	c	-0.42988	1.99894	4.41399	0.01695	6.42988
42	s	0.30964	9.99885	5.65482	0.03668	15.69036
43	h	0.25449	0	0.74452	0.00099	0.74551
44	c	-0.0909	1.99884	4.07529	0.01677	6.0909
45	c	-0.19464	1.99893	4.18024	0.01547	6.19464
46	c	-0.21926	1.99889	4.2043	0.01607	6.21926
47	c	-0.04376	1.99886	4.0295	0.01539	6.04376
48	c	-0.21593	1.99889	4.201	0.01604	6.21593
49	c	-0.19613	1.99894	4.18072	0.01646	6.19613
50	h	0.22348	0	0.77459	0.00193	0.77652
51	h	0.22486	0	0.77338	0.00176	0.77514
52	h	0.22381	0	0.77437	0.00182	0.77619
53	h	0.23345	0	0.76355	0.003	0.76655
54	c	-0.61605	1.99924	4.60703	0.00979	6.61605
55	h	0.22438	0	0.77416	0.00147	0.77562
56	h	0.2168	0	0.78185	0.00135	0.7832
57	h	0.2235	0	0.77505	0.00145	0.7765
58	h	0.49403	0	0.50483	0.00114	0.50597
Total		0	83.96507	169.3186	0.7163	254

Table S3: Summary of Natural population analysis of BTA.2F complex.

No	Atom	Natural charge	Natural population			
			Core	Valence	Rydberg	Total
1	c	-0.19702	1.99896	4.18155	0.01651	6.19702
2	c	-0.20318	1.99896	4.18823	0.01598	6.20318
3	c	-0.26007	1.99889	4.24342	0.01776	6.26007
4	c	0.41154	1.99877	3.55486	0.03482	5.58846
5	c	-0.13596	1.99882	4.11467	0.02247	6.13596
6	c	-0.196	1.99886	4.17974	0.0174	6.196
7	h	0.2329	0	0.76551	0.00159	0.7671
8	h	0.23466	0	0.76357	0.00176	0.76534
9	h	0.23277	0	0.76119	0.00604	0.76723
10	h	0.23597	0	0.76147	0.00256	0.76403
11	o	-0.71149	1.99971	6.70201	0.00977	8.71149
12	c	0.14032	1.99895	3.82703	0.0337	5.85968
13	h	0.28723	0	0.70709	0.00568	0.71277
14	n	-0.65297	1.9991	5.63864	0.01523	7.65297
15	h	0.42439	0	0.56702	0.0086	0.57561
16	n	-0.51806	1.99909	5.49538	0.02359	7.51806
17	h	0.54272	0	0.45239	0.00489	0.45728
18	c	0.33122	1.99911	3.63277	0.0369	5.66878
19	s	0.33327	9.99888	5.63066	0.03719	15.66673
20	c	-0.42381	1.99894	4.40757	0.0173	6.42381
21	c	0.14513	1.99886	3.82899	0.02703	5.85487
22	n	-0.59963	1.99917	5.58274	0.01773	7.59963
23	h	0.25611	0	0.74295	0.00093	0.74389
24	c	-0.09428	1.99884	4.07865	0.0168	6.09428
25	c	-0.19255	1.99893	4.17613	0.01749	6.19255
26	c	-0.21719	1.99888	4.20136	0.01694	6.21719
27	c	-0.04245	1.99886	4.02828	0.01531	6.04245
28	c	-0.22042	1.99889	4.20545	0.01608	6.22042
29	c	-0.19527	1.99894	4.18088	0.01546	6.19527
30	h	0.23422	0	0.75923	0.00656	0.76578
31	h	0.2251	0	0.77073	0.00417	0.7749
32	h	0.2242	0	0.77401	0.00178	0.7758
33	h	0.22313	0	0.77495	0.00192	0.77687
34	c	-0.61551	1.99924	4.60649	0.00978	6.61551
35	h	0.22067	0	0.77792	0.00141	0.77933
36	h	0.21748	0	0.78113	0.00139	0.78252
37	h	0.22541	0	0.7731	0.00149	0.77459
38	c	0.4015	1.99904	3.55932	0.04013	5.5985
39	n	-0.52039	1.99915	5.50262	0.01861	7.52039
40	c	0.25323	1.99892	3.71915	0.0287	5.74677
41	c	-0.32628	1.99912	4.30799	0.01917	6.32628
42	s	0.52583	9.99877	5.43249	0.04291	15.47417
43	h	0.28155	0	0.71729	0.00116	0.71845

44	c	-0.11141	1.99884	4.09567	0.01689	6.11141
45	c	-0.15475	1.99894	4.14025	0.01556	6.15475
46	c	-0.21593	1.99889	4.20082	0.01622	6.21593
47	c	0.01354	1.99888	3.97236	0.01522	5.98646
48	c	-0.20629	1.99889	4.19129	0.01612	6.20629
49	c	-0.154	1.99895	4.13859	0.01646	6.154
50	h	0.23336	0	0.76459	0.00205	0.76664
51	h	0.23665	0	0.76169	0.00166	0.76335
52	h	0.2357	0	0.76258	0.00172	0.7643
53	h	0.24478	0	0.75287	0.00235	0.75522
54	c	-0.62175	1.99923	4.61247	0.01005	6.62175
55	h	0.23566	0	0.76301	0.00133	0.76434
56	h	0.22321	0	0.77553	0.00126	0.77679
57	h	0.23419	0	0.76448	0.00132	0.76581
58	h	0.53846	0	0.45678	0.00476	0.46154
59	f	-0.63917	1.99996	7.63559	0.00362	9.63917
60	f	-0.61028	1.99995	7.60625	0.00407	9.61028
Total		0	87.96518	183.2515	0.78337	272

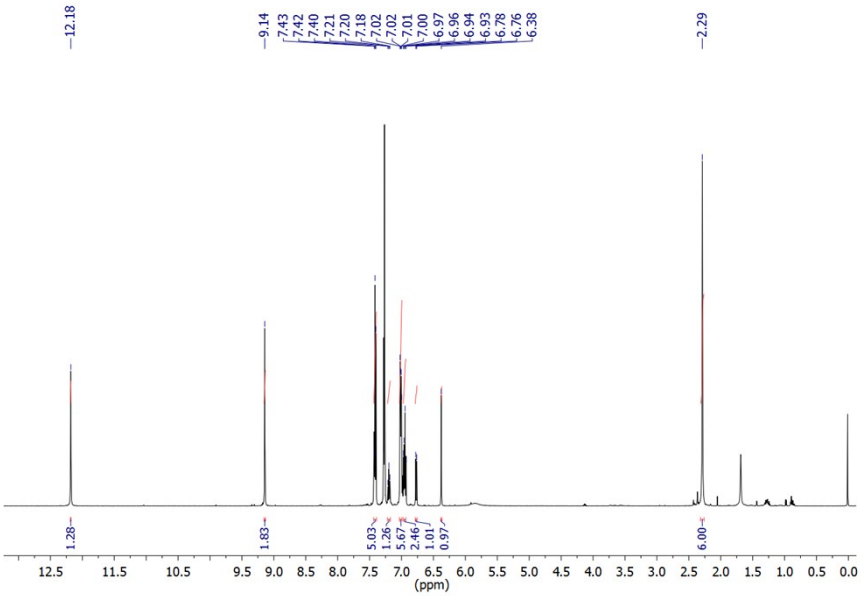


Figure S8: ^{1}H NMR of 2-(bis((4-(p-tolyl)thiazol-2-yl)amino)methyl)phenol (**BTA**).

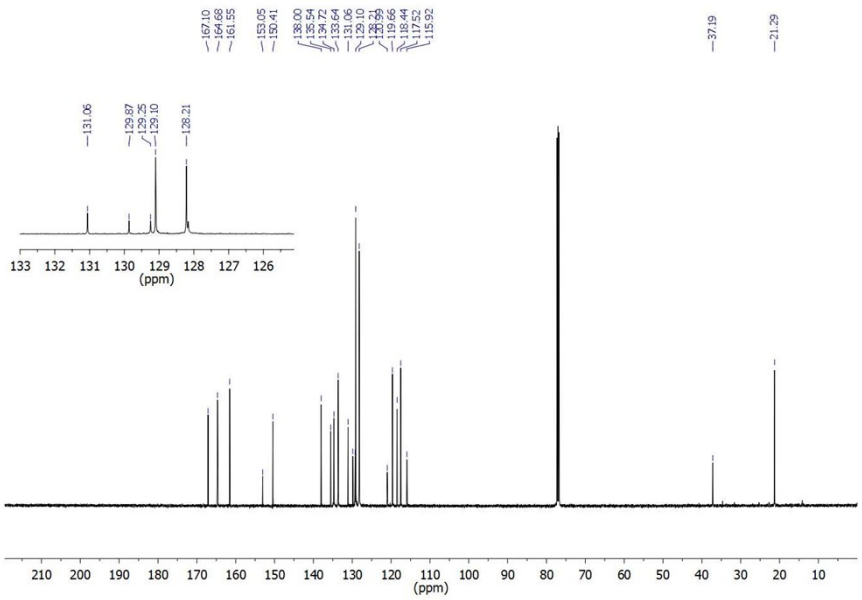


Figure S9: ^{13}C of 2-(bis((4-(p-tolyl)thiazol-2-yl)amino)methyl)phenol (**BTA**).

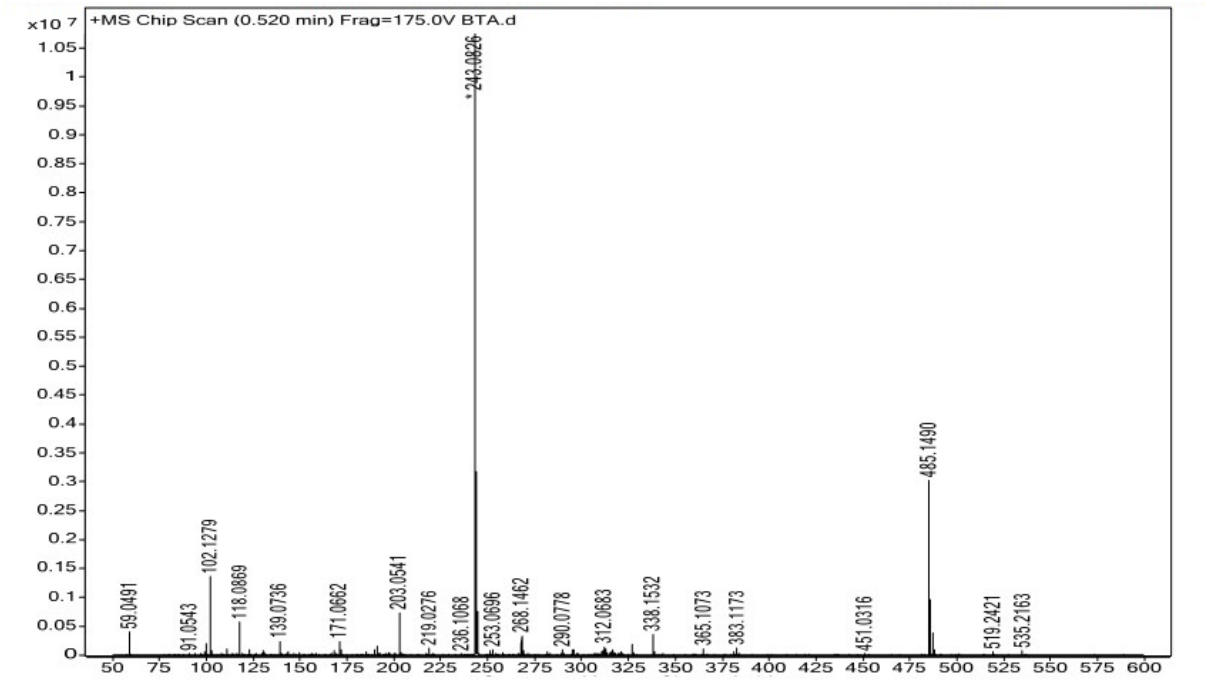


Figure S10: HRMS (ESI-QTOF) spectra of **BTA**.

References:

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