Electronic Supplementary Information

High Affinity Host-Guest Complex of Cucurbit[7]uril with a Bis(thiazolium) Salt

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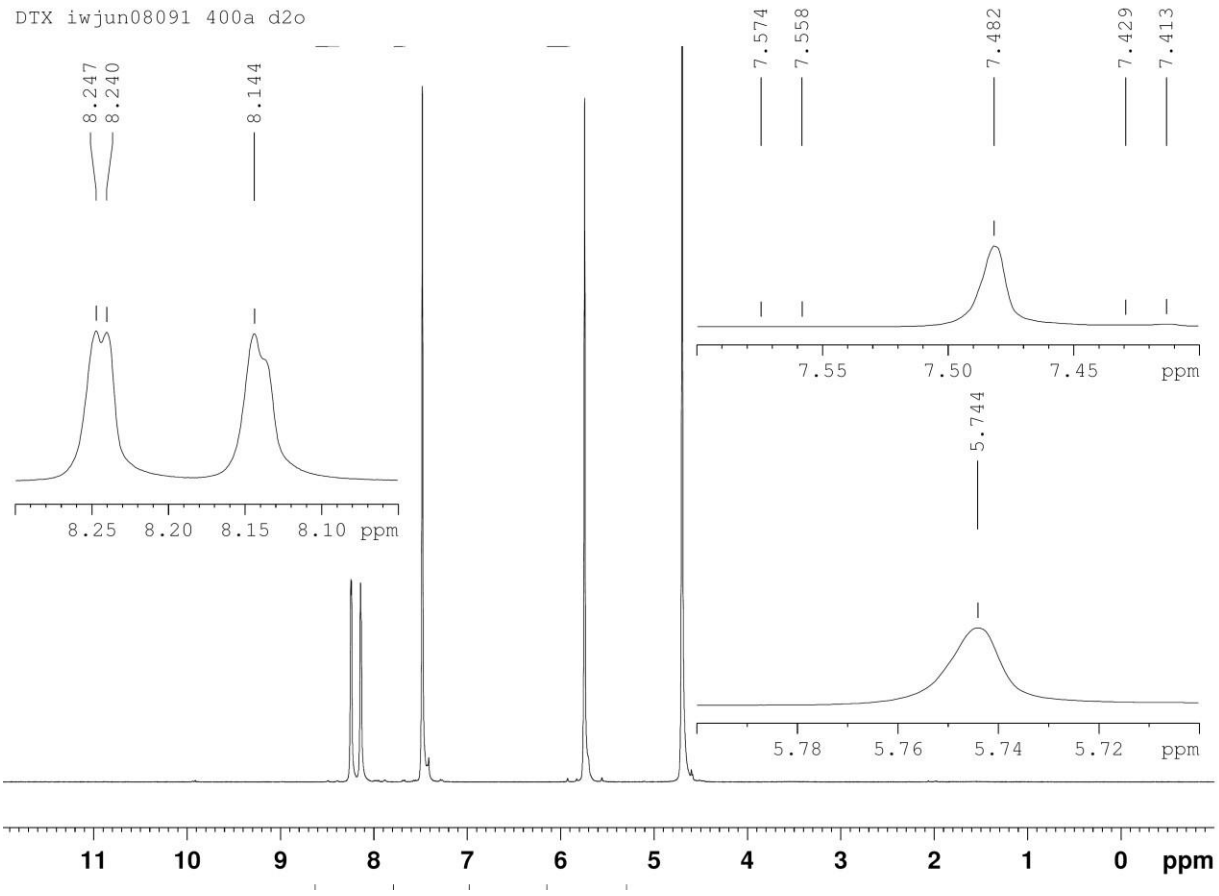

Figure S1. ^{1}H NMR spectrum of [BTX]Br_2 in D_2O (400 MHz). Note: the H2 proton (9.91 ppm) has exchanged with deuterium from D_2O.

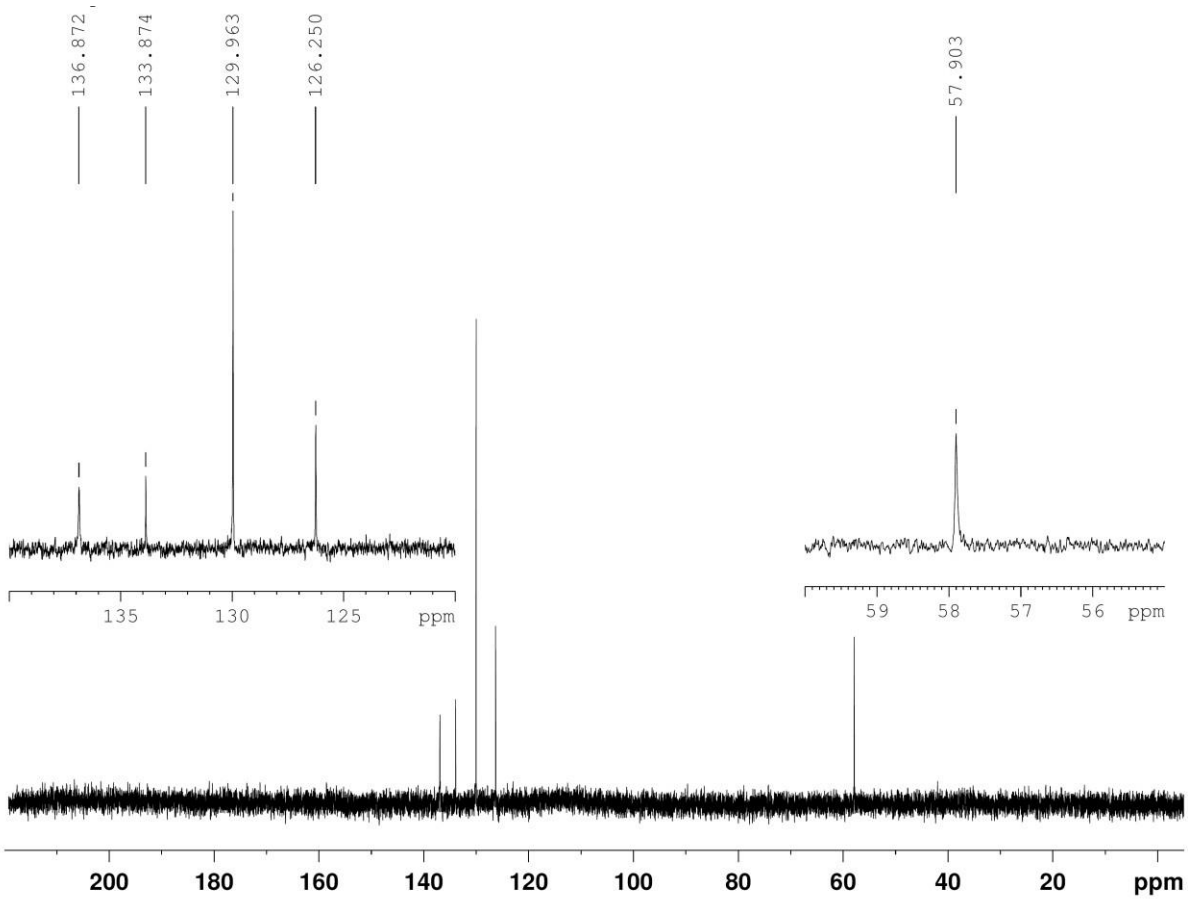

Figure S2. ^{13}C NMR spectrum of [BTX]Br_2 in D_2O (100 MHz). Note: the C1 and C4 carbons on the *p*-xylyl ring are not observed.

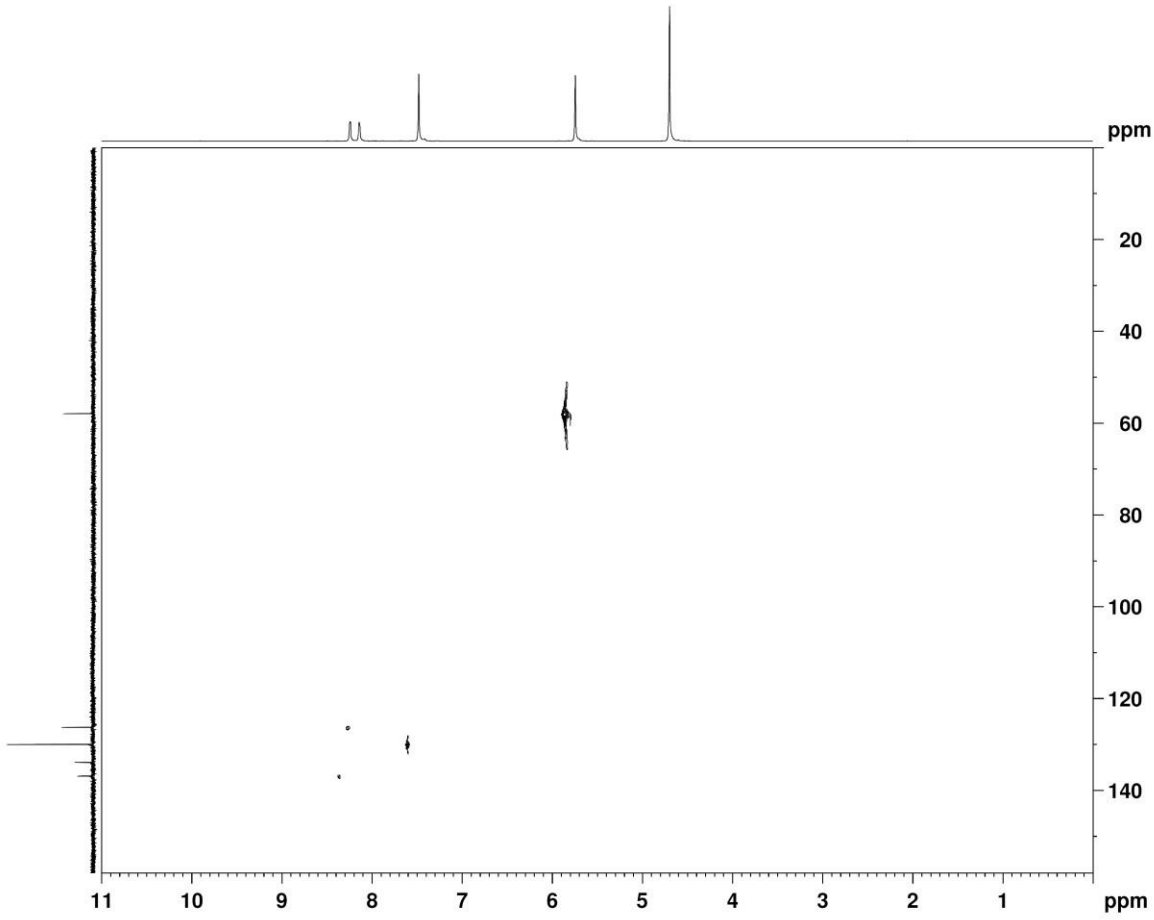

Figure S3. HSQC spectrum of [BTX]Br_2 in D_2O. Note: there is no coupling between the C2 carbon and H2 proton resonances as the proton has been exchanged with deuterium from the D_2O.

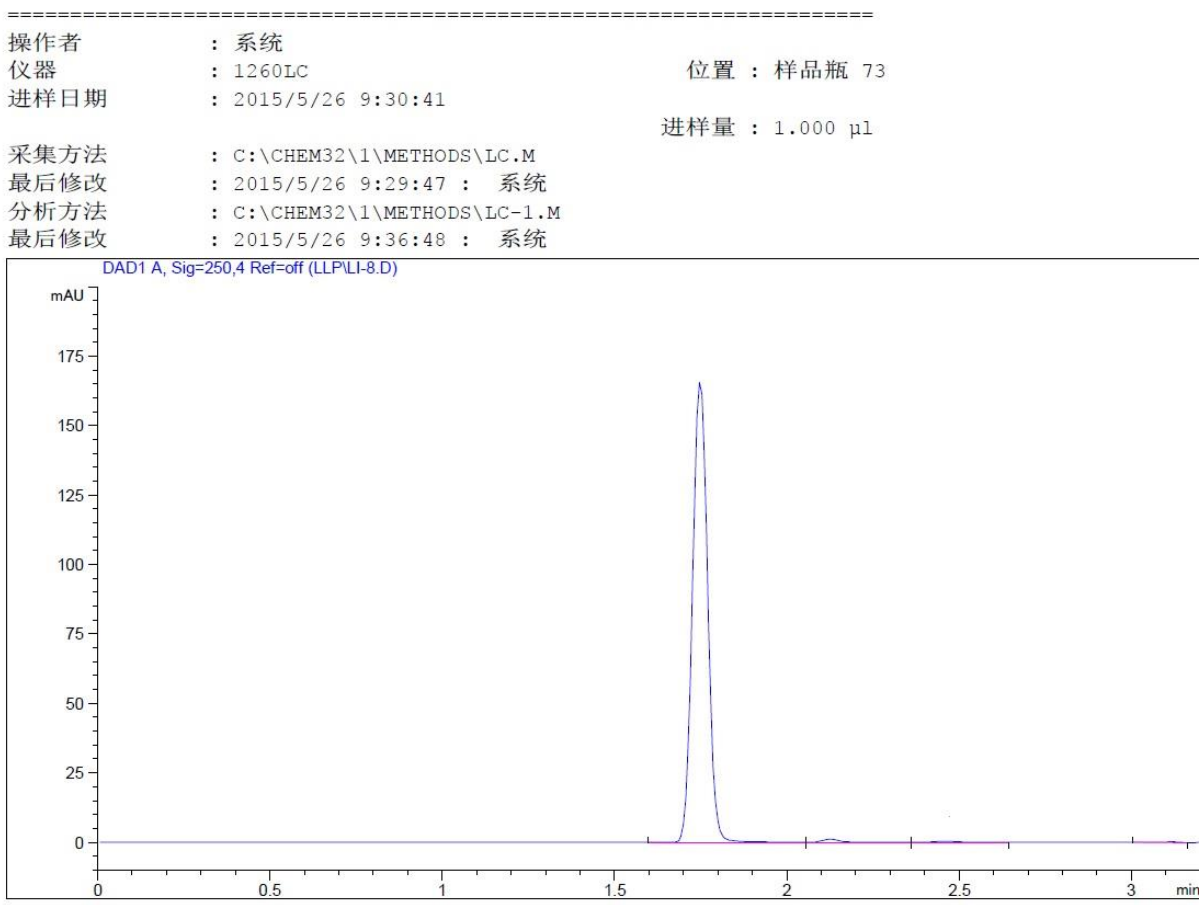

Figure S4. HPLC chromatogram of [BTX]Br_2. Stationary phase: C18; Mobile phase: MeOH:H_2O = 10: 90 (1.0g TTAB (Tetradecyltrimethylammonium bromide) and 2 mL glacial acetic acid was added into 500ml H_2O). Temperature: 35 ℃; Flow rate: 1 mL/min; Detection wave length: 250 nm. The PDA integration shows of a purity higher than 98% (consistent with ^{1}H and ^{13}C NMR spectra).

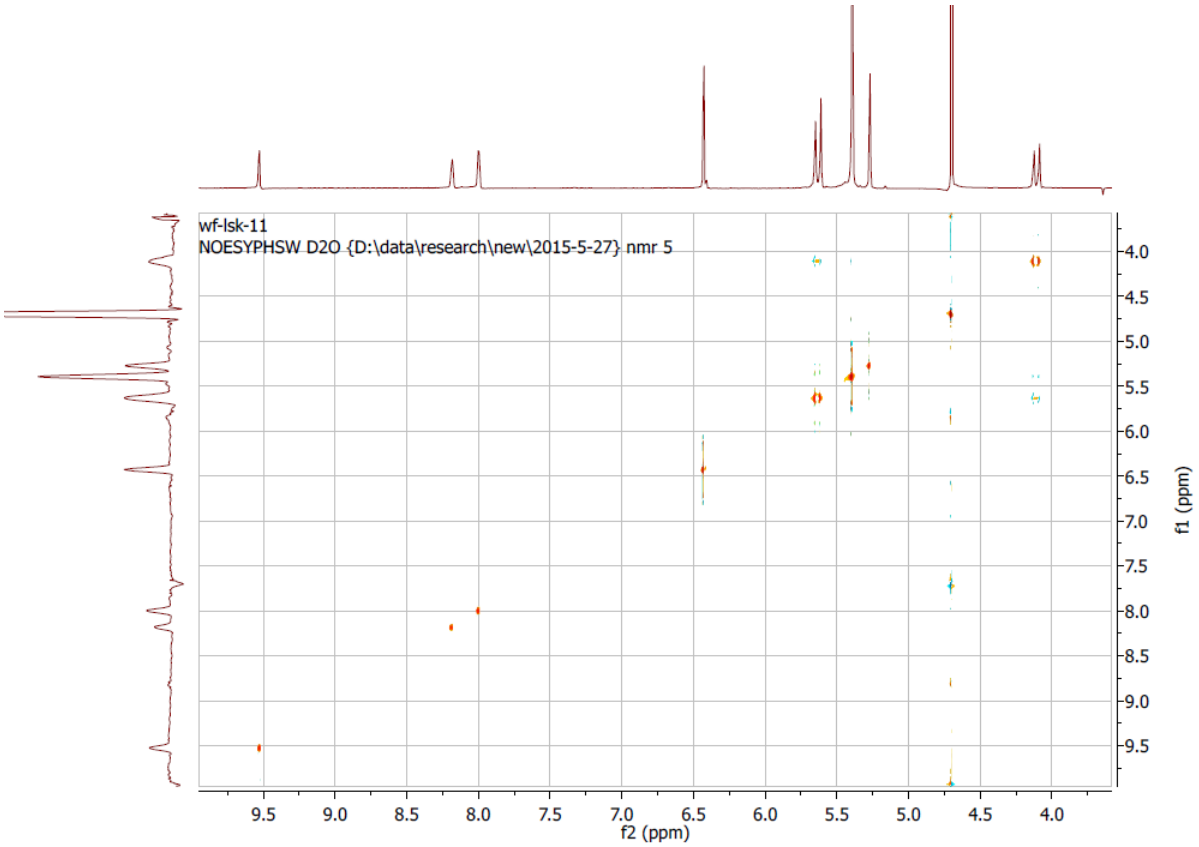

Figure S5. NOESY spectrum of BTX^{2+}-CB[7] complex showing no correlation between the host and guest protons due to the protons of the host CB[7] pointing "externally". This data supports the formation of inclusion complex (instead of "exclusion").

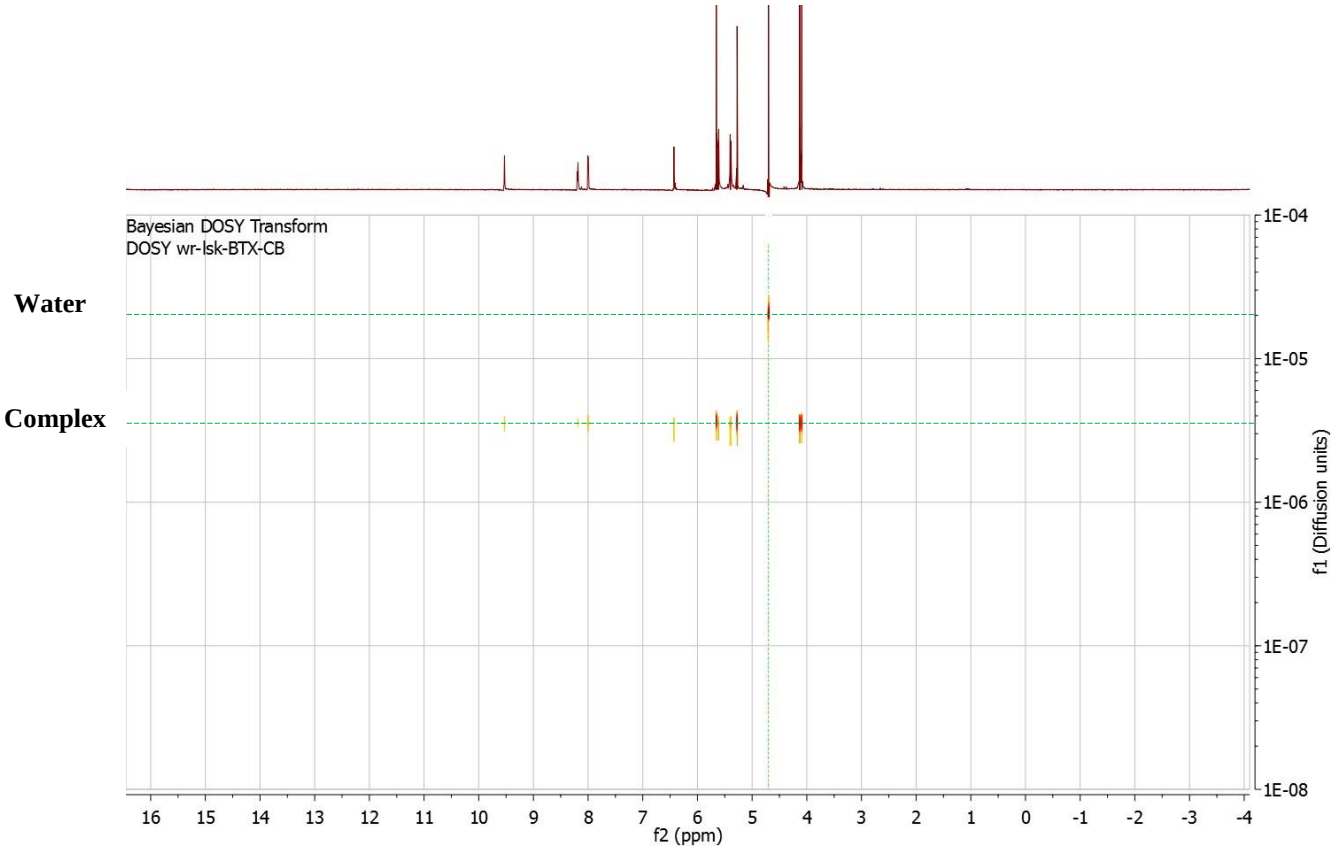

Figure S6. DOSY spectrum of BTX^{2+}-CB[7] complex showing identical diffusion coefficients for both the host and the guest protons attests the strong supramolecular complexation.

Calculation of Host-Guest Binding Constant by Competitive ^{1}H NMR spectroscopy
(see Figure S4 below)

$[TMAF]_{total}$ = 1.82 mM (total integration of the free and bound trimethyl group protons is 9)

$[TMAF]_{bound}$ = 1.82 ×5.22/11 = 0.86 mM;

$[TMAF]_{free}$ = 1.82-0.86 = 0.96 mM;

$[BTX^{2+}]_{bound}$ = 1.82 ×3.70/4 = 1.68 mM (Integration for bound-guest 4 aromatic proton is about 3.70);

$[BTX^{2+}]_{free}$ = 1.82 ×81.93/4 = 37.28 mM (Integration for free-guest 4 aromatic proton is 81.93);

Therefore, $[CB[7]\text{-}BTX^{2+}]_{complex} = [BTX^{2+}]_{bound}$ = 1.68 mM;

$[CB[7]\text{-}TMAF]_{complex} = [TMAF]_{bound}$ = 0.86 mM;

As $K_{CB[7]\text{-}BTX}/K_{CB[7]\text{-}TMAF} = [CB[7]\text{-}BTX^{2+}]_{complex} \times [TMAF]_{free}/([CB[7]\text{-}TMAF]_{complex} \times [BTX^{2+}]_{free})$ = 1.68 ×0.96/(0.86 ×37.28) = 0.05 and $K_{CB[7]\text{-}TMAF} = (3.31 \pm 0.62) \times 10^{11}$ M^{-1};

Therefore, $K_{CB[7]\text{-}BTX} = (1.66 \pm 0.31) \times 10^{10}$ M^{-1}.

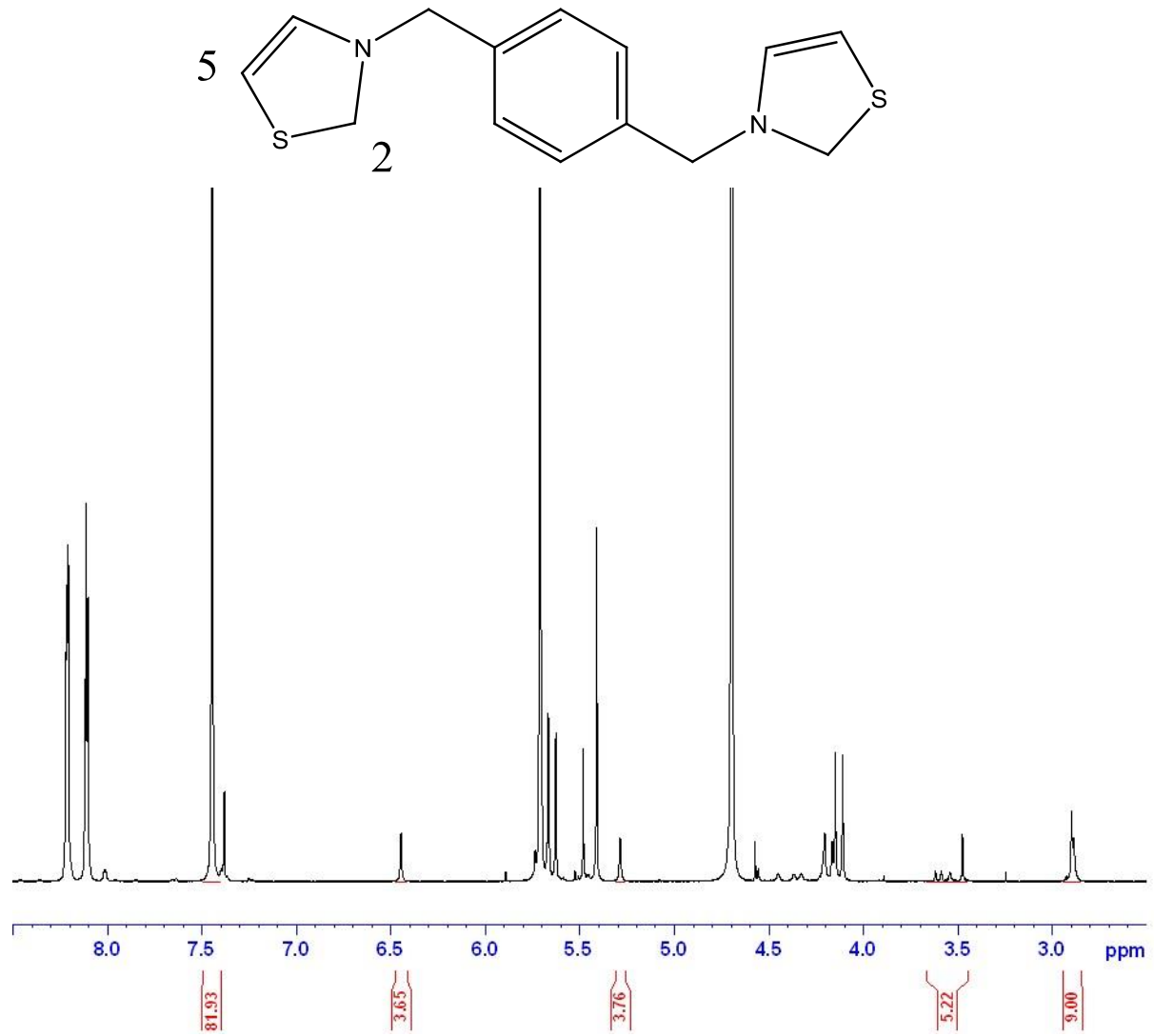

Figure S7. ^{1}H NMR spectrum for competitive NMR binding constant calculation.

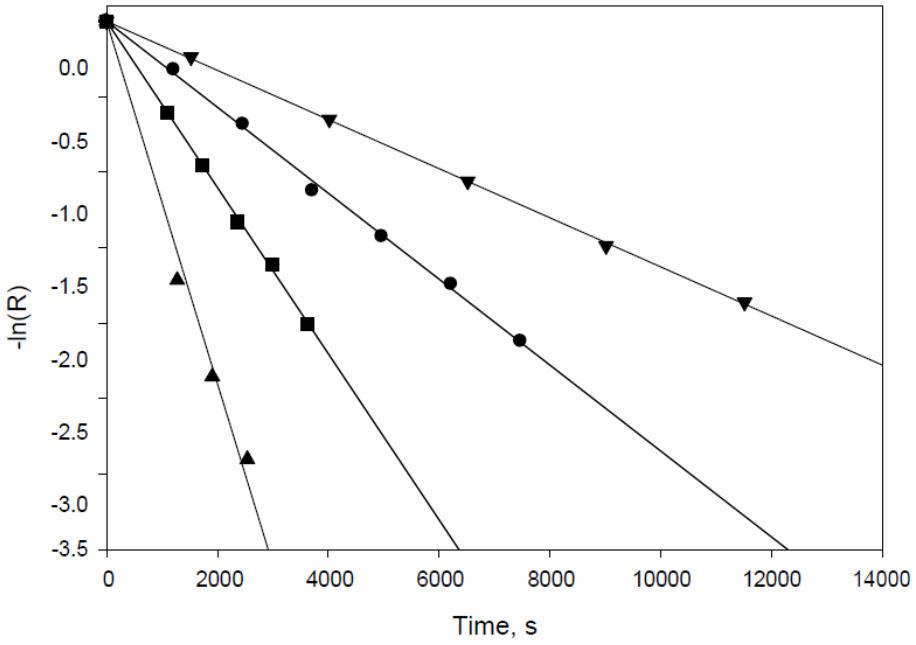

Figure S8. Kinetic plot for the C(2)-H/D exchange reaction of BTX^{2+} as a function of pD at 298K: pD = 4.26 (●), 4.54 (■), 4.81 (▲), and 3.96 (▼).

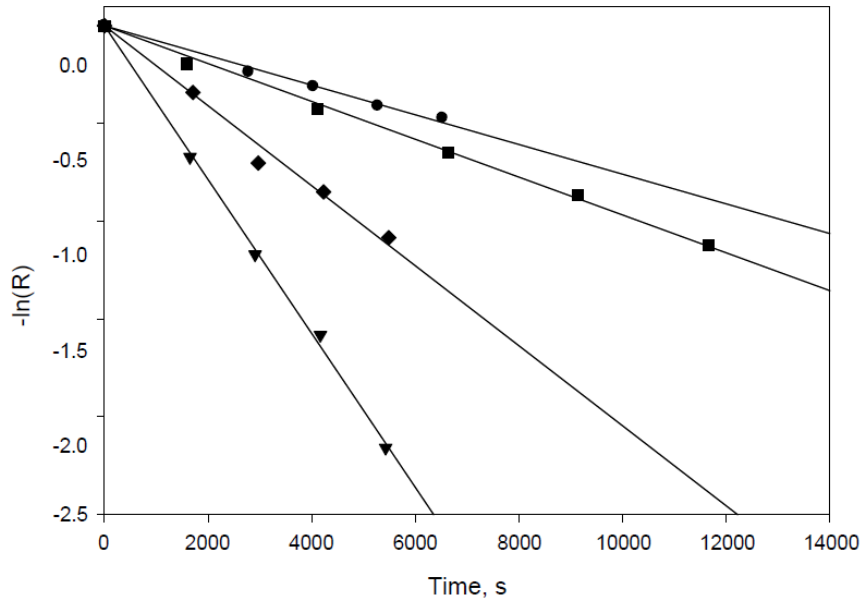

Figure S9. Kinetic plot for the C(2)-H/D exchange reaction of $\{BTX•CB[7]\}^{2+}$ as a function of pD at 298K: pD = 4.31 (●), 4.45 (■), 4.71(▲), and 5.06(▼).

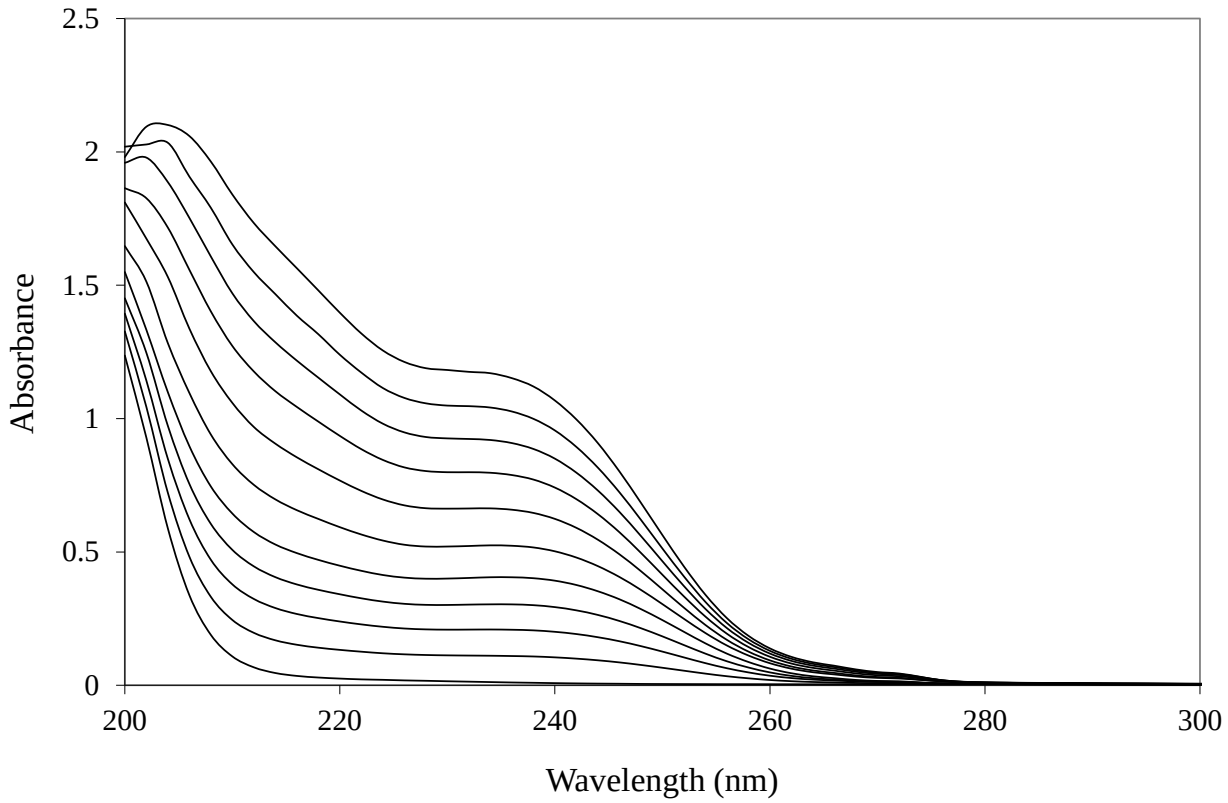

Figure S10. UV-visible spectra of continuous titration of BTX^{2+}-[CB[7]] $^{+}$(with [CB[7]] + $[BTX^{2+}]$ fixed at a constant concentration of 0.10 mM, and the ratio of [CB[7]]/[CB[7]+BTX^{2+}]) varies from 0, 0.1, 0.2 … 1.0 from top to the bottom)

Energy-minimization calculations

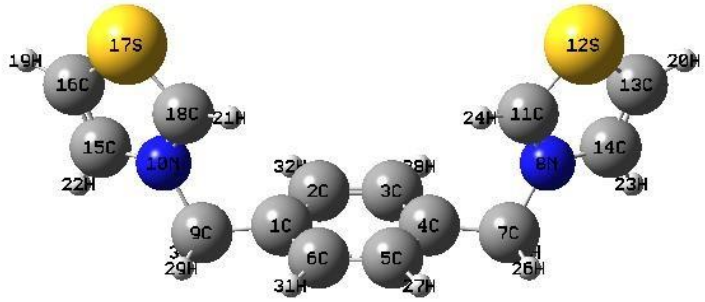

Figure S11. Energy-minimized structure of BTX^{2+}

Table S1. Atomic coordinates for BTX^{2+} (total energy = -5599.6459 au)

Standard orientation:

Center Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	C	-1.390724	-1.462665	0.076006
2	C	-0.690026	-1.037504	-1.050962
3	C	0.689916	-1.037515	-1.051045
4	C	1.390744	-1.462693	0.075836
5	C	0.695881	-1.853832	1.205562
6	C	-0.695732	-1.853807	1.205651
7	C	2.899275	-1.617101	0.021887
8	N	3.621739	-0.292442	-0.069611
9	C	-2.899265	-1.617078	0.022242
10	N	-3.621740	-0.292446	-0.069453
11	C	3.252826	0.797648	0.559557
12	S	4.314832	2.077734	0.335689
13	C	5.316705	1.096009	-0.661877
14	C	4.816337	-0.140847	-0.781177
15	C	-4.816350	-0.140977	-0.781030
16	C	-5.316729	1.095891	-0.661923
17	S	-4.314843	2.077796	0.335456
18	C	-3.252832	0.797751	0.559533
19	H	-6.211281	1.469406	-1.104460
20	H	6.211247	1.469603	-1.104367
21	H	-2.366439	0.844566	1.149327
22	H	-5.217149	-0.962832	-1.326359
23	H	5.217137	-0.962604	-1.326652
24	H	2.366438	0.844358	1.149365
25	H	3.191387	-2.174715	-0.852302
26	H	3.275631	-2.118517	0.898462
27	H	1.217848	-2.197240	2.074844

28	H	1.216230	-0.747796	-1.937286
29	H	-3.275528	-2.118320	0.898957
30	H	-3.191459	-2.174873	-0.851804
31	H	-1.217600	-2.197195	2.075000
32	H	-1.216441	-0.747780	-1.937141

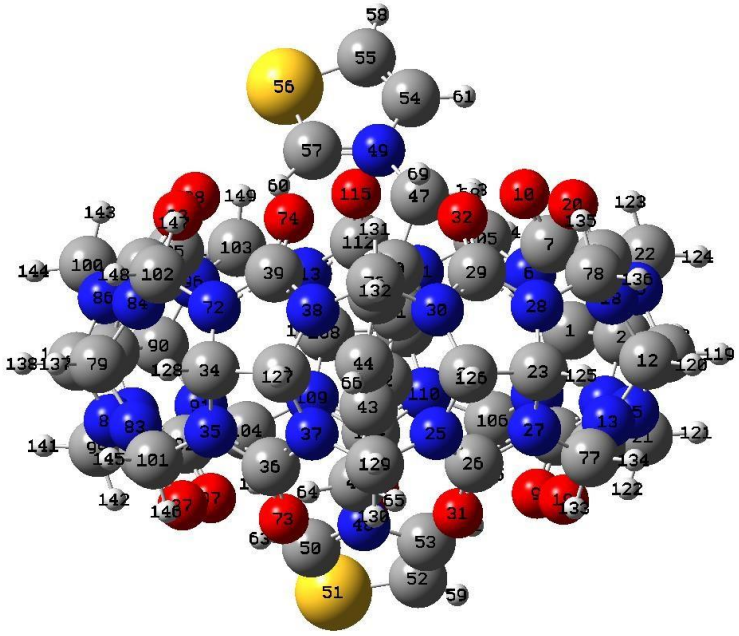

Figure S12. Energy minimized structure for {BTX•CB[7]} with atom labeled with center numbers (see table below)

Table S2. Atomic coordinates for {BTX•CB[7]} from energy-minimization calculations (total energy = -5599.6459 au)

Standard orientation:

Center Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	C	-2.847019	5.017749	-0.051681
2	C	-1.393959	5.639074	-0.068118
3	N	-0.842138	5.110387	-1.296194
4	C	-1.737791	4.361467	-2.020043
5	N	-2.920025	4.328297	-1.317764
6	N	-2.810989	4.170806	1.123996
7	C	-1.617107	4.229633	1.797118
8	N	-0.813823	5.130024	1.154413
9	O	-1.546326	3.892077	-3.121626
10	O	-1.354570	3.642848	2.832195
11	C	2.246995	5.444755	-0.061880
12	C	3.626126	4.669420	-0.044977

13	N	3.543843	3.853853	-1.235783
14	C	2.343508	3.964903	-1.887892
15	N	1.610638	4.938814	-1.258272
16	N	1.638967	5.029992	1.179941
17	C	2.387512	4.112188	1.876060
18	N	3.571678	3.944880	1.205473
19	O	2.022325	3.372830	-2.899826
20	O	2.083431	3.610639	2.938970
21	C	0.428004	5.509506	-1.873288
22	C	0.431361	5.590979	1.742951
23	C	5.786173	1.760469	0.036181
24	C	6.105607	0.209404	0.079865
25	N	5.498012	-0.275622	-1.139939
26	C	4.818558	0.696433	-1.828423
27	N	5.025176	1.889835	-1.188417
28	N	5.039005	1.966069	1.256068
29	C	4.800504	0.805283	1.950245
30	N	5.457362	-0.213074	1.300526
31	O	4.207505	0.540520	-2.867295
32	O	4.183100	0.706096	2.989345
33	C	5.083988	-3.324515	0.130142
34	C	3.978543	-4.461976	0.130533
35	N	3.327409	-4.269605	-1.146079
36	C	3.796233	-3.181580	-1.837364
37	N	4.829756	-2.637398	-1.119646
38	N	4.771348	-2.573328	1.323440
39	C	3.649169	-3.026663	1.971162
40	C	0.470636	0.409885	1.644572
41	C	-0.487600	0.733637	0.696908
42	C	-0.306131	0.385391	-0.636005
43	C	0.847331	-0.275314	-1.037366
44	C	1.782150	-0.631558	-0.075493
45	C	1.592020	-0.303000	1.253837
46	C	1.185882	-0.613193	-2.488138
47	C	0.424785	0.949772	3.057399
48	N	0.125509	-0.176313	-3.431985
49	N	-0.745279	0.464205	3.873928
50	C	-0.757853	-1.002237	-3.944102
51	O	-1.853279	-0.225304	-4.942724
52	C	-1.077824	1.284783	-4.665538
53	C	-0.035903	1.153606	-3.837083
54	C	-1.321742	1.309618	4.824522
55	C	-2.236660	0.676555	5.564669
56	O	-2.442303	-0.945087	5.037440
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60	H	-0.924028	-1.540888	3.236587
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62	H	0.628189	1.907942	-3.478672
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76	C	5.593202	-1.525315	1.904202
77	C	4.660427	3.139628	-1.824781
78	C	4.692848	3.255939	1.819777
79	C	0.617547	-5.768262	0.004260
80	C	-0.957537	-5.736425	-0.089773
81	N	-1.184775	-4.991320	-1.312392
82	C	-0.024714	-4.571583	-1.911359
83	N	1.023098	-5.128428	-1.226385
84	N	0.880137	-4.999292	1.202488
85	C	-0.260549	-4.509450	1.791793
86	N	-1.333141	-5.041779	1.114900
87	O	0.053721	-3.887529	-2.917444
88	O	-0.320155	-3.804632	2.778853
89	C	-4.204423	-4.067507	-0.244055
90	C	-5.128136	-2.782178	-0.261027
91	N	-4.671904	-2.073172	-1.439319
92	C	-3.641624	-2.708955	-2.082409
93	N	-3.375033	-3.874364	-1.412834
94	N	-3.528609	-3.953829	1.027513
95	C	-3.862309	-2.822868	1.721086
96	N	-4.822152	-2.156369	1.005831
97	O	-3.110319	-2.354313	-3.117333
98	O	-3.441393	-2.518714	2.819338
99	C	-2.473558	-4.866066	-1.966726
100	C	-2.681553	-4.963669	1.631551
101	C	2.372300	-5.167407	-1.761312
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107	C	-5.285249	2.329926	-0.120264
108	C	-5.742802	0.816605	-0.190870
109	N	-5.107256	0.353230	-1.407992
110	N	-4.577861	2.510573	-1.365037
111	N	-4.460812	2.350407	1.070278
112	C	-4.393256	1.134725	1.706061
113	N	-5.212539	0.265127	1.033019
114	C	-4.432261	1.346550	-2.077406
115	O	-3.778745	0.900716	2.725468
116	O	-3.876604	1.234127	-3.149101
117	H	-3.633113	5.752072	0.032182
118	H	-1.381510	6.717765	-0.073344
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122	H	0.412760	5.182392	-2.899143
123	H	0.412792	5.306317	2.781010
124	H	0.469918	6.667642	1.650533
125	H	6.664698	2.385829	0.011058
126	H	7.159408	-0.018738	0.101444

127	H	6.094159	-3.700775	0.163119
128	H	4.382458	-5.459156	0.210454
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130	H	5.416795	-1.544169	-2.738904
131	H	5.285878	-1.426143	2.931801
132	H	6.629334	-1.828862	1.846935
133	H	4.378483	2.899362	-2.836156
134	H	5.522583	3.793382	-1.820089
135	H	4.421005	3.081475	2.847397
136	H	5.560950	3.899241	1.764251
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143	H	-2.609268	-4.715488	2.676473
144	H	-3.150524	-5.930009	1.508203
145	H	2.738577	-6.180839	-1.670664
146	H	2.310333	-4.884105	-2.798467
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153	H	-3.699553	3.270095	2.724485
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156	H	-4.928866	4.504662	-1.779357
157	H	-6.102607	3.028698	-0.035122
158	H	-6.812350	0.686056	-0.240007

Reference

1. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A. Jr.; Vreven, T.; Kudin, N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03, Revision C.02, Gaussian*, Pittsburgh, PA 2004.