Supplementary Information for

Selective Host-Guest Chemistry: Self-Assembly and Conformational Preferences of m-Xylene Macrocycles Probed by Ion-Mobility Spectrometry Mass Spectrometry

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S1. Tables of *m/z*, assignments, and CCSs

* indicates MS peaks with weak intensity.

-- *m/z* difference greater than 50 ppm.

Table S1. MXT

Observed *m/z*	Assignment	Theoretical *m/z*	*m/z* difference (ppm)	CCS (Å^2)
Negative Mode				
355.1044	$[MXT–H]^-$	355.1051	-1.97	114
391.0810	$[MXT+Cl]^-$	391.0818	-2.05	118
418.0996	$[MXT+NO_3]^-$	418.1008	-2.87	120
711.2139	$[2MXT–H]^-$	711.2181	-5.91	171
747.1905	$[2MXT+Cl]^-$	747.1947	-5.60	179
774.2086	$[2MXT+NO_3]^-$	774.2137	-6.58	181
Positive Mode				
357.1211	$[MXT+H]^+$	357.1208	0.84	109
379.1019	$[MXT+Na]^+$	379.1027	-2.11	112
395.0755	$[MXT+K]^+$	395.0766	-2.78	113
419.0416	$[MXT–H+Zn]^+$	419.0343	17.4	108
713.2325	$[2MXT+H]^+$	713.2337	-1.68	173
735.2115	$[2MXT+Na]^+$	735.2156	-5.57	174
775.1543	$[2MXT–H+Zn]^+$	775.1472	9.15	175
With added Zn^{2+}				
419.0408	$[MXT–H+Zn]^+$	419.0343	15.51	108
775.1532	$[2MXT–H+Zn]^+$	775.1472	7.74	175
1069.35	$[3MXT+H]^+$	1069.3470	5.14	299

Table S2. MXU

Observed *m/z*	Assignment	Theoretical *m/z*	*m/z* difference (ppm)	CCS (Å^2)
Negative Mode				
323.1487	$[MXU–H]^-$	323.1508	-6.4	113
359.1246	$[MXU+Cl]^-$	359.1275	-8.07	115
401.1578	$[MXU–H+DMSO]^-$	401.1647	-17.2	120
437.1338	$[MXU+DMSO+Cl]^-$	437.1414	-17.3	121
521.2025*	$[3MXU+2Cl]^{2-}$	521.2070	-8.6	308
599.2123*	$[3MXU+2DMSO+2Cl]^{2-}$	599.2205	-13.6	316
647.3055	$[2MXU–H]^-$	647.3094	-6.02	164
683.2823	$[2MXU+Cl]^-$	683.2861	-5.56	171
710.3006	$[2MXU+NO_3]^-$	710.3051	-6.33	173
Positive Mode				
325.1654	$[MXU+H]^+$	325.1665	-3.38	106
347.1490	$[MXU+Na]^+$	347.1484	1.70	107
363.1229	$[MXU+K]^+$	363.1223	1.65	107
425.1720*	$[MXU+DMSO+Na]^+$	425.1623	22.8	128
441.1305	$[MXU+DMSO+K]^+$	441.1363	-13.14	133
506.2243	$[3MXU+H+K]^{2+}$	506.2235	1.58	224
649.3335	$[2MXU+H]^+$	649.3251	12.9	169
660.3135*	$[4MXU+H+Na]^{2+}$	660.3160	-3.70	265
668.3071	$[4MXU+H+K]^{2+}$	668.3030	6.10	270
671.3160	$[2MXU+Na]^+$	671.3070	13.4	170
687.2745	$[2MXU+K]^+$	687.2810	-9.40	170
710.3175	$[4MXU+DMSO+2Na]^{2+}$	710.3140	4.90	278
718.3056	$[4MXU+DMSO+Na+K]^{2+}$	718.3010	6.40	283
749.25*	$[2MXU+DMSO+Na]^+$	749.3210	--	177
830.3893	$[5MXU+H+K]^{2+}$	830.3825	8.18	316
880.3872	$[5MXU+DMSO+Na+K]^{2+}$	880.3805	7.38	323
992.4721	$[6MXU+H+K]^{2+}$	992.4615	10.68	369
995.4772	$[3MXU+Na]^{2+}$	995.4656	11.65	220
1011.446	$[3MXU+K]^+$	1011.440	5.93	218
1042.4464	$[6MXU+DMSO+Na+K]^{2+}$	1042.459	-12.08	368
1095.450*	$[3MXU–H+DMSO+2Na]^+$	1095.462	-10.9	230
1111.419	$[3MXU–H+DMSO+Na+K]^+$	1111.435	-14.0	225

Table S3. MXS

Observed *m/z*	Assignment	Theoretical *m/z*	*m/z* difference (ppm)	CCS (Å^2)
Negative Mode				
427.1411	$[MXS–H]^-$	427.1406	1.17	119 133
463.1164	$[MXS–Cl]^-$	463.1173	-1.94	129
490.1354	$[MXS+NO_3]^-$	490.1363	-1.84	129
541.1323	$[MXS+DMSO+Cl]^-$	541.1312	2.03	138
855.2865	$[2MXS–H]^-$	855.2891	-3.03	196
Positive Mode				
429.1558	$[MXS+H]^+$	429.1563	-1.16	119
448.1292*	$[2MXS+H+K]^{2+}$	448.1342	-11.16	210
451.1377	$[MXS+Na]^+$	451.1382	-1.11	123
467.1115	$[MXS+K]^+$	467.1122	-1.49	125
545.1163*	$[MXS+DMSO+K]^+$	545.1261	-17.9	149
662.2036	$[3MXS+H+K]^{2+}$	662.2085	-7.40	262
876.2775	$[4MXS+H+K]^{2+}$	876.2825	-5.71	318
879.2854	$[2MXS+Na]^+$	879.2867	-1.48	192
	$[4MXS+2Na]^{2+}$			318
895.2594	$[2MXS+K]^+$	895.2606	-1.34	196
	$[4MXS+2K]^+$			312
1090.3507	$[5MXS+H+K]^{2+}$	1090.357	-5.78	357
1307.4333	$[3MXS+Na]^+$	1307.435	-1.30	252
	$[6MXS+2Na]^{2+}$			412
1323.4035	$[3MXS+K]^+$	1323.409	-4.15	249
With $(NH_4)_2SO_4$				
525.1210	$[MXS+H+SO_4]^-$	525.1080	24.7	136
953.2524	$[2MXS+H+SO_4]^-$	953.2565	-4.30	206

Additional Figures

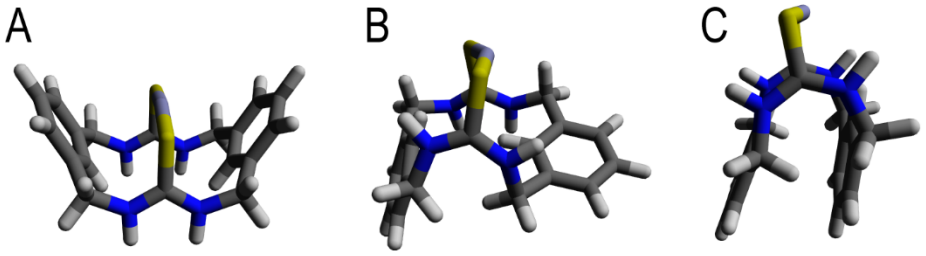

Fig. S1. DG generated, B3LYP optimized structures of MXT·Zn^{2+} complexes. Note that to maximize the interactions between Zn and S atoms, the two thioureas should be in the *syn* configuration. The amines could be in any configuration, but the low energy structures have them in either *trans-trans* (lowest), *cis-cis* or a mixture of *trans-trans* and *cis-cis*.

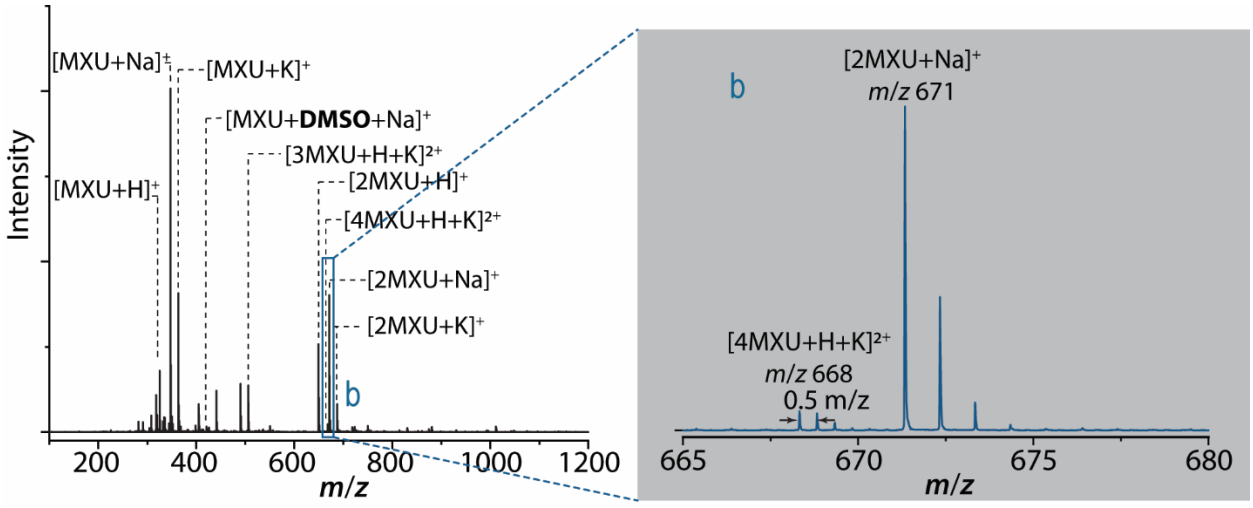

Fig. S2. An example of isotope spacing used in assignments of *m/z* mass spectral peaks.

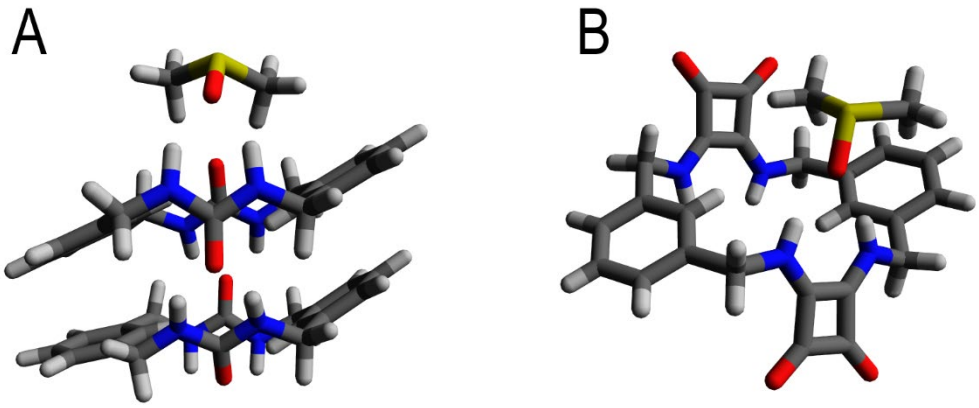

Fig. S3. (A) QM structure of 2MXU·DMSO. (B) X-ray crystal structure of MXS·DMSO.

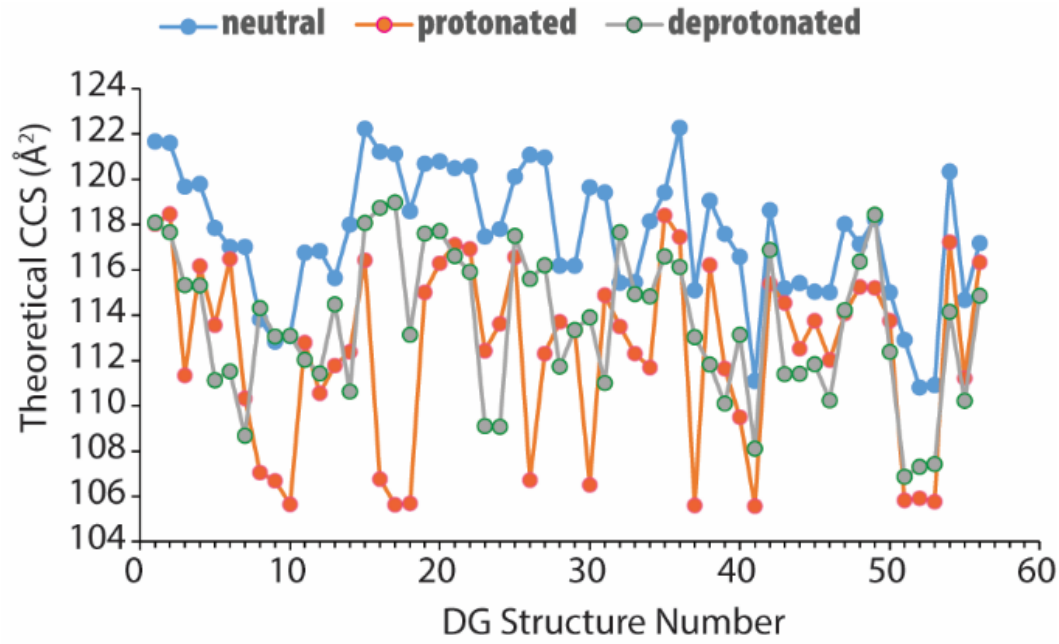

Fig. S4. Theoretical CCSs of 56 distinct MXT structures sampled by DG. We created the deprotonated $[M-H]^-$ and $[M+H]^+$ form of each structure and performed geometry optimization using the same protocol described in Section S1.

The general trend suggests that protonation tends to compact the structures more than deprotonation. The result appears to be consistent with our experimental data reported in section S2, in which the experimental CCSs in positive mode are often smaller than those in negative mode.

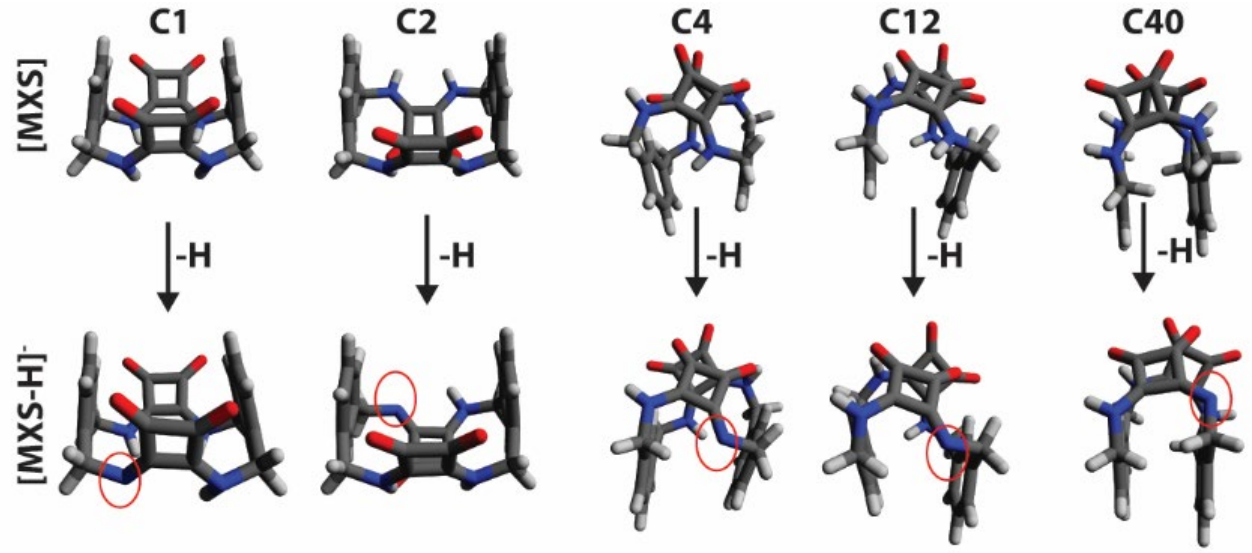

Fig. S5. Neutral and deprotonated structures of MXS obtained from DG and QM calculations. Because the four amine protons are not equivalent, we generated different versions of the deprotonated structures and reported those with the smallest CCSs.

Table S4. Tuning parameters (positive polarity) used in this work.

Parameter	Value
Pre-IMS Zone	
Source: gas temperature	300 °C
Source: drying gas	5 l/min
Source: nebulizer pressure	13 psi
Source: capillary	3500 V
Optics I: fragmentor	250 V
IM front funnel: high pressure funnel delta	110 V
IM front funnel: high pressure RF	180 V
IM front funnel: trap funnel delta	160 V
IM front funnel: trap funnel RF	180 V
IM front funnel: trap funnel exit	10 V
IM trap: trap entrance grid low	82 V
IM trap: trap entrance grid delta	2 V
IM trap: trap entrance	79 V
IM trap: trap exit	76 V
IM trap: trap exit grid 1 low	72 V
IM trap: trap exit grid 1 delta	6 V
IM trap: trap exit grid 2 low	71 V
IM trap: trap exit grid 2 delta	13 V
Acquisition: trap fill time	1000 µs
Acquisition: trap release time	100 µs
Post-IMS Zone	
IM drift tube: drift tube exit	210 V
IM rear funnel: rear funnel entrance	200 V
IM rear funnel: rear funnel RF	130 V
IM rear funnel: rear funnel exit	35 V
IM rear funnel: IM Hex entrance	42 V
IM rear funnel: IM Hex delta	8 V
Optics 1: Oct entrance lens	32 V
Optics 1: Lens 1	28.3 V
Optics 1: Lens 2	15.8 V
Quad: Quad DC	26.6 V
Quad: postfilter DC	26.5 V
Cell: gas flow	22 psi
Cell: cell entrance	25.6 V
Cell: Hex DC	24.2 V
Cell: Hex delta	-9 V
Cell: Hex2 DC	15 V
Cell: Hex2 DV	-3 V
Optics 2: Hex3 DC	11.8 V
Extractor: ion focus	5.6 V

Table S5. Tuning parameters (negative polarity) used in this work.

Parameter	Value
Pre-IMS Zone	
Source: gas temperature	300 °C
Source: drying gas	5 l/min
Source: nebulizer pressure	9 psi
Source: capillary	3500 V
Optics I: fragmentor	300 V
IM front funnel: high pressure funnel delta	-150 V
IM front funnel: high pressure RF	200 V
IM front funnel: trap funnel delta	-180 V
IM front funnel: trap funnel RF	200 V
IM front funnel: trap funnel exit	-10 V
IM trap: trap entrance grid low	-97 V
IM trap: trap entrance grid delta	-10 V
IM trap: trap entrance	-91 V
IM trap: trap exit	-90 V
IM trap: trap exit grid 1 low	-87.7 V
IM trap: trap exit grid 1 delta	-5 V
IM trap: trap exit grid 2 low	-87 V
IM trap: trap exit grid 2 delta	10.5 V
Acquisition: trap fill time	1000 µs
Acquisition: trap release time	150 µs
Post-IMS Zone	
IM drift tube: drift tube exit	-250 V
IM rear funnel: rear funnel entrance	-240 V
IM rear funnel: rear funnel RF	180 V
IM rear funnel: rear funnel exit	-43 V
IM rear funnel: IM Hex entrance	-41 V
IM rear funnel: IM Hex delta	8 V