Supplementary Material (ESI) for New Journal of Chemistry

SUPPORTING INFORMATION FOR:

Exploring a new kind of aromatic hydrogen bond: hydrogen bonding to all-metal aromatic species

Xingbang Hu, Haoran Li[a], Wanchun Liang and Shijun Han

Department of Chemistry, Zhejiang University, Hangzhou 310027, P. R. China

Supporting Information Available:

1. Z-MATRIX of Al_4^{2-} … H-Y calculated at B3LYP/6-311++G**, B3LYP/aug-cc-pvdz, MP2/6-311++G** and MP2/aug-cc-pvdz respectively (ANGSTROMS AND DEGREES)

1) B3LYP/6-311++G**

(A) Al_4^{2-}

Al						
Al	1	2.592974				
Al	1	2.593011	2	90.004284		
Al	3	2.592979	1	89.995721	2	-0.007778

(B) Al_4^{2-}…CH_4

Al						
Al	1	2.593165				
Al	1	2.593008	2	90.008224		
Al	3	2.592514	1	89.983758	2	-0.007307
C	4	5.692881	3	77.481122	1	-78.152929
H	5	1.091648	4	17.051234	3	42.100551
H	5	1.092402	4	124.877178	3	16.477311
H	5	1.092713	4	95.654204	3	-102.298147
H	5	1.092929	4	106.106532	3	145.347867

(C) Al_4^{2-}…NH_3

[a] Author to whom correspondence should be addressed. Electronic mail: lihr@zju.edu.cn

Supplementary Material (ESI) for New Journal of Chemistry

Al						
Al	1	2.591551				
Al	1	2.591058	2	89.948382		
Al	3	2.590379	1	90.047783	2	0.086784
N	3	4.477663	1	78.854757	2	-74.231629
H	5	1.020447	3	83.304406	1	11.496775
H	5	1.020717	3	43.381527	1	-105.928142
H	5	1.020643	3	70.828561	1	118.089147

(D) Al_4^{2-}…H_2O

Al						
Al	1	2.589484				
Al	1	2.588121	2	90.192846		
Al	2	2.587997	1	89.854623	3	-0.088316
O	1	4.170322	2	72.177905	4	-81.032601
H	5	0.969487	1	38.749495	2	-84.553320
H	5	0.970845	1	64.573131	2	70.664492

(E) Al_4^{2-}…HF

Al						
Al	1	2.585005				
Al	1	2.585005	2	90.010466		
Al	3	2.585067	1	89.991388	2	0.013629
F	1	4.079965	2	71.534942	4	-70.502817
H	1	3.257659	2	66.627824	4	-64.408763

(F) Al_4^{2-}…HCl

Al						
Al	1	2.585062				
Al	1	2.585058	2	89.999027		
Al	3	2.585061	1	90.001098	2	0.000044
Cl	1	4.424854	2	73.022885	4	-72.219252
H	1	3.235615	2	66.461524	4	-64.170577

(G) Al_4^{2-}…HBr

Al						
Al	1	2.584040				
Al	1	2.584047	2	90.002916		
Al	2	2.584075	1	89.998024	3	-0.004811
Br	1	4.325943	2	72.625985	4	-71.769659
H	1	2.947268	2	64.004991	4	-60.819089

2) B3LYP/aug-cc-pvdz

(A) Al_4^{2-}

Al						
Al	1	2.605691				
Al	1	2.605692	2	90.001788		
Al	2	2.605691	1	89.998227	3	-0.001759

(B) Al_4^{2-}…CH_4

Al						
Al	1	2.607589				
Al	1	2.606502	2	90.007741		

Supplementary Material (ESI) for New Journal of Chemistry

Al	3	2.605219	1	89.977447	2	0.021892
C	4	5.262363	3	79.292790	1	-88.519167
H	5	1.097447	4	13.919243	3	34.347493
H	5	1.098649	4	111.022478	3	119.756488
H	5	1.098494	4	119.774470	3	-9.454789
H	5	1.098771	4	96.466704	3	-126.392756

(C) Al_4^{2-}…NH_3

Al						
Al	1	2.605349				
Al	1	2.604248	2	89.947735		
Al	3	2.604298	1	90.077774	2	0.031317
N	2	4.527851	1	74.179971	3	73.471926
H	5	1.023876	2	54.830986	1	62.669048
H	5	1.024095	2	85.302169	1	-46.196264
H	5	1.023858	2	56.123761	1	-154.663110

(D) Al_4^{2-}…H_2O

Al						
Al	1	2.603708				
Al	1	2.602381	2	90.108216		
Al	2	2.602021	1	89.917828	3	-0.192883
O	1	4.175928	2	71.882129	4	-80.289208
H	5	0.971523	1	38.217775	2	-83.732389
H	5	0.972873	1	65.086018	2	70.806195

(E) Al_4^{2-}…HF

Al						
Al	1	2.599866				
Al	1	2.599859	2	90.003044		
Al	3	2.599871	1	89.997330	2	0.000088
F	3	4.090629	1	71.473330	2	-70.434459
H	2	3.266948	1	66.553684	3	64.308909

(F) Al_4^{2-}…HCl

Al						
Al	1	2.598239				
Al	1	2.598235	2	89.999562		
Al	3	2.598239	1	90.000625	2	0.000022
Cl	1	4.437644	2	72.984582	4	-72.175191
H	1	3.241963	2	66.383582	4	-64.067515

(G) Al_4^{2-}…HBr

Al						
Al	1	2.596118				
Al	1	2.596122	2	90.001560		
Al	2	2.596145	1	89.999127	3	-0.000265
Br	1	4.323210	2	72.532379	4	-71.656846
H	1	2.946614	2	63.869071	4	-60.621211

3) MP2/6-311++G**

(A) Al_4^{2-}

Al						

Supplementary Material (ESI) for New Journal of Chemistry

Al						
Al	1	2.584890				
Al	1	2.584890	2	90.002069		
Al	2	2.584890	1	89.997931	3	0.000000

(B) Al_4^{2-}…CH_4

Al						
Al	1	2.588369				
Al	1	2.588611	2	89.970259		
Al	2	2.587908	1	90.023139	3	-0.033565
C	4	4.621135	2	74.453017	1	75.048230
H	5	1.090867	4	22.804708	2	-46.624387
H	5	1.092948	4	116.232059	2	30.179039
H	5	1.093015	4	121.690696	2	-108.182313
H	5	1.092896	4	86.576248	2	140.613529

(C) Al_4^{2-}…NH_3

Al						
Al	1	2.588418				
Al	1	2.591044	2	90.002899		
Al	2	2.588426	1	90.055386	3	0.148763
N	2	4.096665	1	74.537104	3	74.110683
H	5	1.019493	2	54.226545	1	58.180255
H	5	1.019105	2	91.843458	1	-47.047091
H	5	1.019492	2	54.352778	1	-152.258192

(D) Al_4^{2-}…H_2O

Al						
Al	1	2.585453				
Al	1	2.585350	2	90.068482		
Al	2	2.585368	1	90.029026	3	-0.002084
O	1	3.872322	2	70.508134	4	-78.519444
H	5	0.967007	1	46.328356	2	-70.223842
H	5	0.969076	1	57.857247	2	77.171384

(E) Al_4^{2-}…HF

Al						
Al	1	2.583751				
Al	1	2.583746	2	90.000614		
Al	3	2.583748	1	89.999447	2	-0.001109
F	3	4.026401	1	71.287158	2	-70.202043
H	3	3.220117	1	66.350866	2	-64.031056

(F) Al_4^{2-}…HCl

Al						
Al	1	2.584115				
Al	1	2.584117	2	89.996895		
Al	3	2.584116	1	90.003089	2	-0.000576
Cl	4	4.381238	3	72.850215	1	-72.028277
H	4	3.239761	3	66.498068	1	-64.226626

(G) Al_4^{2-}…HBr

Al						
Al	1	2.583327				

Supplementary Material (ESI) for New Journal of Chemistry

Al		2.583326	2	89.996313		
Al	2	2.583326	1	90.003687	3	0.000710
Br	4	4.397561	2	72.926808	1	72.111613
H	4	3.124391	2	65.588096	1	63.006013

4) MP2/aug-cc-pvdz

(A) Al_4^{2-}

Al						
Al	1	2.630295				
Al	1	2.630295	2	90.000000		
Al	2	2.630280	1	90.000000	3	-0.002004

(B) $Al_4^{2-}…CH_4$

Al						
Al	1	2.631546				
Al	1	2.631515	2	89.996342		
Al	2	2.631454	1	90.004638	3	-0.002656
C	4	4.730953	2	73.894340	1	73.315986
H	5	1.099265	4	22.927862	2	-48.633343
H	5	1.100800	4	116.179307	2	28.602677
H	5	1.100840	4	122.008242	2	-110.001151
H	5	1.100818	4	86.530954	2	138.870213

(C) $Al_4^{2-}…NH_3$

Al						
Al	1	2.632660				
Al	1	2.633636	2	90.016599		
Al	2	2.632617	1	90.004636	3	0.079046
N	2	4.106864	1	73.221817	3	72.549602
H	5	1.027292	2	54.601638	1	60.427219
H	5	1.027468	2	85.237384	1	-47.430749
H	5	1.027275	2	54.688285	1	-155.259343

(D) $Al_4^{2-}…H_2O$

Al						
Al	1	2.632309				
Al	1	2.632079	2	90.029888		
Al	2	2.632207	1	89.986374	3	-0.135501
O	2	4.013240	1	70.949820	3	72.737582
H	5	0.973826	2	40.953279	1	61.300965
H	5	0.974998	2	64.480719	1	-83.372150

(E) $Al_4^{2-}…HF$

Al						
Al	1	2.629394				
Al	1	2.629394	2	89.995010		
Al	3	2.629394	1	90.005339	2	-0.001983
F	2	4.006151	1	70.856608	3	69.685209
H	3	3.197747	1	65.739457	2	-63.201061

(F) $Al_4^{2-}…HCl$

Al						
Al	1	2.629374				

Al						
Al	3	2.629376	1	89.999029	2	0.000261
Cl	1	4.246374	2	71.965645	4	-70.999486
H	1	3.100009	2	64.907836	4	-62.078555

(G) Al_4^{2-}…HBr

Al						
Al	1	2.628808				
Al	1	2.628809	2	90.001536		
Al	2	2.628811	1	89.998542	3	-0.000394
Br	1	4.255034	2	72.008978	4	-71.050483
H	1	2.981765	2	63.846732	4	-60.590949

2.Z-MATRIX of C_6H_6…H-Y calculated at MP2/6-311++G**(ANGSTROMS AND DEGREES)

(A) C_6H_6

C						
C	1	1.400315				
C	2	1.400313	1	119.975840		
C	3	1.400314	2	119.975767	1	3.093631
C	4	1.400312	3	119.975890	2	-3.098455
C	5	1.400312	4	119.975692	3	3.103557
H	1	1.086737	2	119.983438	3	179.659512
H	2	1.086737	1	119.983515	6	179.657816
H	3	1.086738	2	119.983430	1	-179.661148
H	4	1.086737	3	119.983370	2	179.655067
H	5	1.086737	4	119.983474	3	-179.652069
H	6	1.086738	5	119.983361	4	179.650788

(B) C_6H_6…CH_4

C						
C	1	2.425646				
C	1	2.425645	2	60.000297		
C	2	1.400450	1	89.999636	3	0.009219
C	1	1.400447	2	30.000008	4	-179.970870
C	1	1.400445	2	90.000294	5	179.970134
H	1	1.086821	2	149.999691	5	0.144687
H	2	1.086821	1	149.999858	6	179.822300
H	3	1.086823	1	149.999789	2	-179.832256
H	4	1.086852	2	119.999809	1	179.952614
H	5	1.086854	1	120.000175	2	179.970881
H	6	1.086854	1	120.000178	2	-179.953698
C	1	3.922762	2	71.990983	5	-100.838157
H	13	1.091081	1	88.608355	2	148.280496
H	13	1.091082	1	118.730936	2	-100.270624
H	13	1.091082	1	118.730932	2	36.831725
H	13	1.089623	1	20.929947	2	-31.719478

(C) C_6H_6…NH_3

C						
C	1	2.802351				
C	2	1.400656	1	59.989987		
C	2	1.400672	1	59.990150	3	179.861166
C	1	1.400826	2	59.981092	3	0.054845

Supplementary Material (ESI) for New Journal of Chemistry

C	1	1.400815	2	59.981351	3	-179.915863
H	1	1.086829	6	120.018097	4	179.843056
H	2	1.086423	3	120.008121	5	-179.613042
H	3	1.086703	2	119.959401	1	-179.975950
H	4	1.086700	2	119.959553	1	179.975667
H	5	1.086880	1	119.992110	2	179.774790
H	6	1.086882	1	119.992003	2	-179.774477
N	2	3.619470	1	73.559213	6	-89.984099
H	13	1.015020	2	23.064630	1	-0.000992
H	13	1.014383	2	118.097405	1	65.586663
H	13	1.014383	2	118.103614	1	-65.571075

(D) $C_6H_6…H_2O$

C						
C	1	1.401125				
C	1	1.401130	2	120.021728		
C	2	1.400923	1	119.998113	3	0.466379
C	3	1.400916	1	119.999124	2	-0.468014
C	5	1.401521	3	119.985748	1	0.362400
H	1	1.086884	2	119.992245	4	-179.480594
H	2	1.086670	1	120.037332	3	179.866644
H	3	1.086665	1	120.036815	2	-179.865015
H	4	1.086492	2	120.029624	1	179.949200
H	5	1.086497	3	120.029315	1	-179.946916
H	6	1.086595	5	119.998531	3	179.962803
O	6	3.552474	5	80.377207	3	72.669100
H	13	0.962299	6	9.112609	5	-61.452397
H	13	0.959846	6	111.709269	5	-61.463089

(E) $C_6H_6…HF$

C						
C	1	2.803230				
C	1	1.401905	2	60.028015		
C	2	1.400974	1	59.967787	3	179.958058
C	2	1.401905	1	60.028015	3	0.000000
C	4	1.400892	2	120.032213	1	0.000000
H	1	1.086442	6	120.051664	4	179.872235
H	2	1.086442	4	120.051664	6	-179.872235
H	3	1.086577	1	120.040274	2	179.998421
H	4	1.086411	2	119.962637	1	179.781887
H	5	1.086577	2	120.040274	1	-179.998421
H	6	1.086411	4	120.004790	2	179.781794
H	3	2.506000	1	83.238076	2	66.816898
F	3	3.369732	1	84.868796	2	72.963395

(F) $C_6H_6…HCl$

C						
C	1	2.802535				
C	1	1.401401	2	60.012491		
C	2	1.401009	1	59.984716	3	179.996954
C	2	1.401401	1	60.012399	3	0.000093
C	4	1.400881	2	120.015323	1	0.000096
H	1	1.086542	6	120.019623	4	179.983596

Supplementary Material (ESI) for New Journal of Chemistry

H	2	1.086542	4	120.019833	6	-179.982738
H	3	1.086626	1	120.019188	2	179.989392
H	4	1.086488	2	119.986238	1	179.987422
H	5	1.086626	2	120.019099	1	-179.989055
H	6	1.086488	4	119.998087	2	179.987657
Cl	5	3.830861	2	80.190502	1	-71.692169
H	5	2.620184	2	78.478910	1	-64.355501

(G) C_6H_6…HBr

C						
C	1	2.802340				
C	1	1.401289	2	60.011067		
C	2	1.400938	1	59.986683	3	-179.990252
C	2	1.401291	1	60.011016	3	0.000142
C	4	1.400839	2	120.013437	1	0.000285
H	1	1.086603	6	120.017472	4	179.969149
H	2	1.086603	4	120.017728	6	-179.968338
H	3	1.086684	1	120.017382	2	179.964914
H	4	1.086551	2	119.989260	1	179.982080
H	5	1.086685	2	120.017477	1	-179.964346
H	6	1.086551	4	119.997159	2	179.982624
Br	5	3.987867	2	80.213468	1	-72.216599
H	5	2.643282	2	78.315162	1	-64.410967

3.Z-MATRIX of Al_4Ca…H-Y calculated at MP2/6-311++G**(ANGSTROMS AND DEGREES)

(A) Al_4Ca

Al						
Al	1	2.621070				
Al	1	2.621080	2	89.998486		
Al	2	2.621070	1	90.001730	3	0.000656
Ca	2	3.047822	1	64.534456	3	61.558863

(B) Al_4Ca…CH_4

Al						
Al	1	2.622535				
Al	1	2.622553	2	89.991610		
Al	3	2.622984	1	90.017913	2	-0.026447
Ca	4	3.044781	3	64.585020	1	-61.618621
C	1	4.481061	2	75.107666	4	74.600165
H	6	1.091159	1	84.437105	2	132.811056
H	6	1.090277	1	24.921852	2	-47.197829
H	6	1.091172	1	119.950705	2	-117.745824
H	6	1.091173	1	119.940135	2	23.369340

(C) Al_4Ca…NH_3

Al						
Al	1	2.621338				
Al	1	2.621322	2	89.991116		
Al	2	2.621358	1	90.009419	3	-0.052503
Ca	2	3.044021	1	64.698093	3	61.725206
N	3	4.024255	1	77.538868	2	77.489364
H	6	1.014960	3	57.541082	1	61.599598
H	6	1.014769	3	93.362402	1	-46.301161

Supplementary Material (ESI) for New Journal of Chemistry

H	6	1.014957	3	57.631509	1	-154.185705

(D) $Al_4Ca…H_2O$

Al						
Al	1	2.625599				
Al	1	2.629529	2	89.988202		
Al	3	2.625557	1	89.999533	2	0.000470
Ca	3	3.035381	1	64.336425	2	-61.848036
O	4	3.940804	3	73.654375	1	69.693747
H	6	0.962782	4	32.785719	3	-39.438945
H	6	0.961124	4	127.177662	3	9.425782

(E) $Al_4Ca…HF$

Al						
Al	1	2.630068				
Al	1	2.630033	2	90.007309		
Al	3	2.630353	1	90.000760	2	0.000452
Ca	1	3.041568	2	64.385553	4	-61.350709
F	1	3.935014	2	70.572192	4	69.306355
H	1	3.152671	2	65.423548	4	62.749689

(F) $Al_4Ca…HCl$

Al						
Al	1	2.627426				
Al	1	2.627413	2	90.007683		
Al	3	2.627585	1	89.996558	2	0.001417
Ca	4	3.043314	3	64.455507	1	-61.444404
Cl	4	4.354371	3	72.458199	1	71.566386
H	1	3.242911	2	66.116535	4	63.709702

(G) $Al_4Ca…HBr$

Al						
Al	1	2.627687				
Al	1	2.627739	2	89.993966		
Al	2	2.627391	1	90.000599	3	-0.000022
Ca	1	3.044951	2	64.465585	4	-61.458660
Br	2	4.431149	1	72.753143	3	-71.920669
H	1	3.185825	2	65.961407	4	63.414026

4.Z-MATRIX of $Al_4Mg…H$-Y calculated at MP2/6-311++G**(ANGSTROMS AND DEGREES)

(A) Al_4Mg

Al						
Al	1	2.666822				
Al	1	2.665813	2	90.015326		
Al	3	2.666592	1	90.023454	2	-0.001519
Mg	2	2.793357	1	61.644358	3	57.178005

(B) $Al_4Mg…CH_4$

Al						
Al	1	2.662655				
Al	1	2.668664	2	90.075501		
Al	2	2.668684	1	90.079661	3	0.001513
Mg	3	2.786769	1	62.054353	2	-57.214268

C	1	4.004120	2	70.586012	4	96.000668
H	6	1.091283	1	61.845680	2	142.433950
H	6	1.090976	1	58.948067	2	-77.760669
H	6	1.091078	1	156.362141	2	-143.715725
H	6	1.091283	1	94.079366	2	32.567821

(C) $Al_4Mg…NH_3$

Al						
Al	1	2.668217				
Al	1	2.661064	2	90.097000		
Al	3	2.661131	1	90.057541	2	0.019760
Mg	2	2.768805	1	62.052797	3	58.079712
N	3	3.893400	1	79.676436	2	79.648578
H	6	1.014562	3	58.824958	1	63.610774
H	6	1.014123	3	91.583753	1	-45.963276
H	6	1.014560	3	58.954500	1	-155.511382

(D) $Al_4Mg…H_2O$

Al						
Al	1	2.670190				
Al	1	2.665110	2	90.065968		
Al	2	2.663272	1	90.267948	3	0.158187
O	1	3.744916	2	71.071305	4	-92.656197
H	5	0.961950	1	51.623561	2	-64.178761
H	5	0.960911	1	63.182707	2	72.068614
Mg	3	2.761477	1	63.046830	2	56.858482

(E) $Al_4Mg…HF$

Al						
Al	1	2.686841				
Al	1	2.687178	2	90.007745		
Al	2	2.687202	1	90.007158	3	-0.000034
Mg	4	2.783294	2	61.190309	1	56.574463
F	1	3.841336	2	69.598290	4	68.124925
H	1	3.074286	2	64.131573	4	60.957448

(F) $Al_4Mg…HCl$

Al						
Al	1	2.679275				
Al	1	2.679425	2	89.976762		
Al	2	2.678171	1	90.002760	3	-0.000602
Mg	1	2.788206	2	61.375671	4	-56.909742
Cl	1	4.271991	2	71.777377	4	70.762371
H	1	3.173880	2	65.129327	4	62.356091

(G) $Al_4Mg…HBr$

Al						
Al	1	2.678287				
Al	1	2.678296	2	90.003217		
Al	2	2.678444	1	90.000491	3	-0.000062
Mg	1	2.794225	2	61.373566	4	-56.909205
Br	4	4.296310	2	72.112521	1	-71.302306
H	1	3.092473	2	64.473063	4	61.429922

Supplementary Material (ESI) for New Journal of Chemistry

5.Z-MATRIX of Na_2Al_4…H-Y calculated at MP2/6-311++G**(ANGSTROMS AND DEGREES)

(A) Na_2Al_4

Al						
Al	1	2.636040				
Al	1	2.545887	2	89.965485		
Al	2	2.545884	1	89.964258	3	0.000121
Na	3	3.188977	1	66.639593	2	63.261111
Na	4	3.038575	2	154.240087	1	5.388746

(B) Na_2Al_4…CH_4

Al						
Al	1	2.550430				
Al	1	2.638638	2	89.621628		
Al	3	2.548337	1	90.203703	2	-0.816884
Na	4	3.149989	3	66.208402	1	-62.814742
Na	2	3.029985	1	154.887351	3	0.152961
C	4	4.440568	3	74.537318	1	74.537227
H	7	1.120006	4	23.323849	3	-47.445635
H	7	1.091684	4	93.326159	3	178.238835
H	7	1.091315	4	100.315880	3	67.496591
H	7	1.091336	4	131.963296	3	-61.340190

(C) Na_2Al_4…NH_3

Al						
Al	1	2.621338				
Al	1	2.621322	2	89.991116		
Al	2	2.621358	1	90.009419	3	-0.052503
Ca	2	3.044021	1	64.698093	3	61.725206
N	3	4.024255	1	77.538868	2	77.489364
H	6	1.014960	3	57.541082	1	61.599598
H	6	1.014769	3	93.362402	1	-46.301161
H	6	1.014957	3	57.631509	1	-154.185705

(D) Na_2Al_4…H_2O

Al						
Al	1	2.625599				
Al	1	2.629529	2	89.988202		
Al	3	2.625557	1	89.999533	2	0.000470
Ca	3	3.035381	1	64.336425	2	-61.848036
O	4	3.940804	3	73.654375	1	69.693747
H	6	0.962782	4	32.785719	3	-39.438945
H	6	0.961124	4	127.177662	3	9.425782

(E) Na_2Al_4…HF

Al						
Al	1	2.630068				
Al	1	2.630033	2	90.007309		
Al	3	2.630353	1	90.000760	2	0.000452
Ca	1	3.041568	2	64.385553	4	-61.350709
F	1	3.935014	2	70.572192	4	69.306355
H	1	3.152671	2	65.423548	4	62.749689

Supplementary Material (ESI) for New Journal of Chemistry

(F) Na_2Al_4…HCl

Al						
Al	1	2.627426				
Al	1	2.627413	2	90.007683		
Al	3	2.627585	1	89.996558	2	0.001417
Ca	4	3.043314	3	64.455507	1	-61.444404
Cl	4	4.354371	3	72.458199	1	71.566386
H	1	3.242911	2	66.116535	4	63.709702

(G) Na_2Al_4…HBr

Al						
Al	1	2.627687				
Al	1	2.627739	2	89.993966		
Al	2	2.627391	1	90.000599	3	-0.000022
Ca	1	3.044951	2	64.465585	4	-61.458660
Br	2	4.431149	1	72.753143	3	-71.920669
H	1	3.185825	2	65.961407	4	63.414026