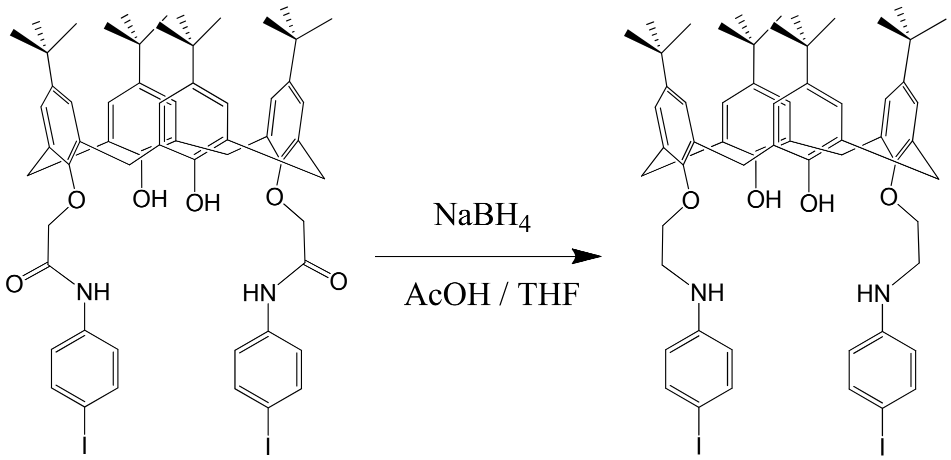
Supplementary information

Highly selective ion probe for Al^{3+} based on Au(I)···Au(I) interactions in a bis-alkynyl calix[4]arene Au(I) isocyanide scaffold

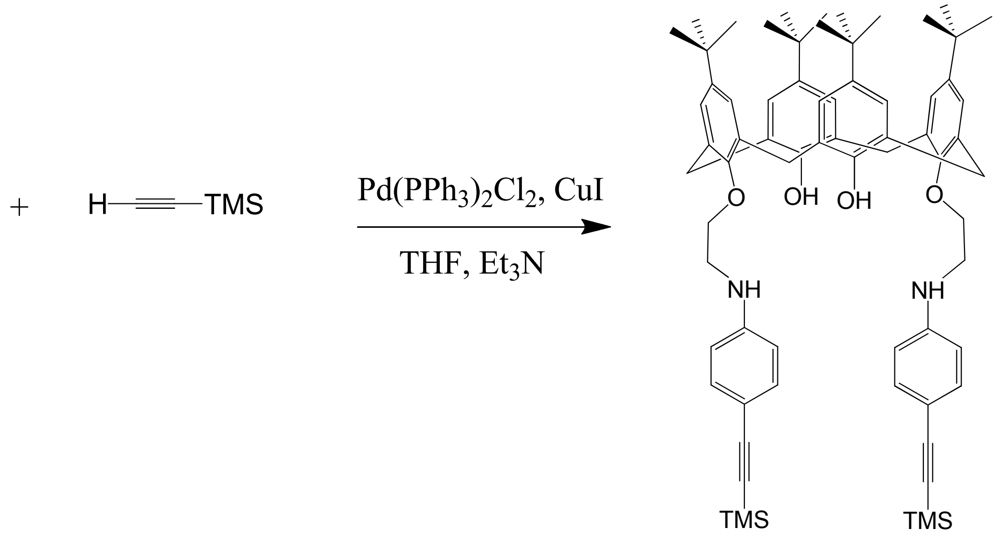
Franky Ka-Wah Hau, Xiaoming He, Wai Han Lam and Vivian Wing-Wah Yam*

Experimental Procedure:

Ligand synthesis and characterization



Calix[4]arene-(OCH_2CH_2NH-$C_6H_4I)_2$



Calix[4]arene-(OCH_2CH_2NH-$C_6H_4C{\equiv}CTMS)_2$

Calix[4]arene-(OCH_2CH_2NH-$C_6H_4I)_2$

To a suspension of calix[4]arene-(OCH_2CONH-$C_6H_4I)_2$[1] (1 g, 0.85 mmol) and $NaBH_4$ (1.2 g, 32 mmol) in THF (30 mL) in an ice-water bath was added acetic acid (2 g, 33 mmol) in THF (10 mL). The reaction mixture was stirred at 0 °C and then refluxed for 6 h. The solvent was removed and the residue was dissolved in dichloromethane (50 mL). The solution was washed with water, dried over anhydrous $MgSO_4$ and filtered. The filtrate was concentrated and purified by column chromatography over silica gel (CH_2Cl_2-hexane, 1:1 v/v) to give the product as a white solid. Yield: 0.45 g, 46 %. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K, Me_4Si): $\delta = 1.18$ (18H, s, -^{t}Bu), 1.25 (18H, s, -^{t}Bu), 3.32 (4H, t, $J = 4.7$ Hz, -OCH_2-), 3.45 (4H, d, $J = 13.4$ Hz, -CH_2-), 4.17 (4H, t, $J = 4.7$ Hz, -$OCH_2C\boldsymbol{H_2}$-), 4.33 (4H, d, $J = 13.4$ Hz, -CH_2-), 6.28 (4H, d, J = 8.7 Hz, -C_6H_4-), 7.04 (4H, s, -C_6H_2-), 7.07 (4H, s, -C_6H_2-), 7.36 (4H, d, J = 8.7 Hz, -C_6H_4-), 8.67 (2H, s, -OH). Positive-ion FAB-MS m/z: 1139 $[M]^+$. Elemental analysis, Anal. Found (%): C, 63.47; H, 6.66; N, 2.31. Calcd. For $C_{60}H_{72}I_2N_2O_4$·THF: C, 63.27; H, 6.37; N, 2.46.

Calix[4]arene-(OCH_2CH_2NH-$C_6H_4C{\equiv}CTMS)_2$

Into a 100–mL two-necked round-bottomed flask was added Calix[4]arene-(OCH_2CH_2NH-$C_6H_4I)_2$ (0.7 g, 0.61 mmol), copper(I) iodide (12 mg, 0.065 mmol), and dichlorobis(triphenylphosphine)palladium(II) (45 mg, 0.065 mmol), followed by a mixture of tetrahydrofuran (30 mL) and triethylamine (10 mL). After the mixture had been stirred for 5 min, trimethylsilylacetylene (0.30 g, 3.05 mmol) was added to the flask under a nitrogen atmosphere. The mixture was stirred for 24 h at room temperature. The mixture was filtered, and the filtrate was evaporated to dryness. The brown residue was purified by column chromatography on silica gel (CH_2Cl_2-hexane, 1:1 v/v) to afford the product as a white solid. Yield: 0.55 g, 85 %.

^{1}H NMR (400 MHz, $CDCl_3$, 298 K, Me_4Si): $\delta = 0.26$ (18H, s, -$SiMe_3$), 1.21(18H, s, -^{t}Bu), 1.25 (18H, s, -^{t}Bu), 3.23 (4H, t, $J = 4.7$ Hz, -OCH_2-), 3.42 (4H, d, $J = 13.4$ Hz, -CH_2-), 4.15 (4H, t, $J = 4.7$ Hz, -$OCH_2C\boldsymbol{H_2}$-), 4.33 (4H, d, $J = 13.4$ Hz, -CH_2-), 6.40 (4H, d, J = 8.7 Hz, -C_6H_4-), 6.99 (4H, s, -C_6H_2-), 7.07 (4H, s, -C_6H_2-), 7.31 (4H, d, J = 8.7 Hz, -C_6H_4-), 8.83 (2H, s, -OH). Positive-ion FAB-MS m/z: 1079 $[M]^+$. Elemental analysis, Anal. Found (%): C, 77.23; H, 8.38; N, 2.39. Calcd. For $C_{70}H_{90}N_2O_4Si_2$·0.5H_2O: C, 77.21; H, 8.40; N, 2.59.

Synthesis of gold(I) alkynyl polymer
[{Calix[4]arene-(OCH_2CH_2NH-$C_6H_4C{\equiv}C)_2$}$Au_2]_\infty$

To the solution of $KAuCl_4$ (37 mg, 0.1 mmol) in CH_3OH (15 mL) and water (1 mL) was added dropwise 2,2'-thiodiethanol (0.5 mL). The stirring was maintained until the solution turned colorless. KF (29 mg, 0.5 mmol) in CH_3OH (2 ml) and Calix[4]arene-(OCH_2CH_2NH-$C_6H_4C{\equiv}CTMS)_2$ (53 mg, 0.05 mmol) in THF (10 mL) were added. The mixture was stirred for 1 h. The yellow precipitate was filtered, washed with water and methanol, and dried under vacuum. **Caution:** *The alkynylgold(I) polymer is potentially explosive and should be handled with great caution.*

Synthesis and characterization of complexes 1-2

Complex 1

To a solution of [{calix[4]arene-(OCH_2CONH-$C_6H_4C{\equiv}C)_2$}Au_2]$_\infty$[1] (100 mg, 0.074 mmol) in dichloromethane was added a solid sample of 2,6-dimethylphenyl isocyanide (20 mg, 0.156 mmol) under a nitrogen atmosphere, and the reaction mixture was stirred at room temperature for 1 h. The solvent was then removed under reduced pressure and the residue was recrystallized from dichloromethane-diethyl ether to give **1** as a white solid. Yield: 65 mg, 54 %. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K, Me_4Si): δ = 1.09 (18H, s, -^{t}Bu), 1.28 (18H, s, -^{t}Bu), 2.45 (12H, s, -CH_3), 3.51 (4H, d, J = 13.4 Hz, -CH_2-), 4.22 (4H, d, J = 13.4 Hz, -CH_2-), 4.58 (4H, s, -OCH_2C-), 6.90 (4H, s, -C_6H_2-), 7.00 (4H, s, -C_6H_2-), 7.17(4H, d, J = 4.9 Hz, -C_6H_4-), 7.29 (4H, d, J = 4.9 Hz, -C_6H_4-),7.32 (6H, m, -C_6H_3-), 8.23 (2H, s, -OH), 10.18 (2H, s, -NH). IR (KBr disk/cm^{-1}): 1692 *v*(C=O), 2210 *v*(N≡C). Positive-ion ESI-MS: m/z 1486 [M-L]$^+$, 1617 [M]$^+$, 1813 [M+Au]$^+$. Elemental analysis, Anal. Found (%): C, 58.70; H, 5.51; N, 3.25. Calcd. For $C_{82}H_{86}Au_2N_4O_6{\cdot}CH_2Cl_2$: C, 58.56; H, 5.21; N, 3.29.

Complex 2

This was prepared according to the procedure for **1** except [{calix[4]arene-(OCH_2CH_2NH-$C_6H_4C{\equiv}C)_2$}Au_2]$_\infty$ (60 mg, 0.045 mmol) was used instead of [{calix[4]arene-(OCH_2CONH-$C_6H_4C{\equiv}C)_2$}Au_2]$_\infty$. Recrystallization by the diffusion of diethyl ether vapor into a dichloromethane solution of the complex gave **2** as a white solid. Yield: 40 mg, 56 %. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K, Me_4Si): δ = 1.16 (18H, s, -^{t}Bu), 1.24 (18H, s, -^{t}Bu), 2.43 (12H, s, -CH_3), 3.19 (4H, t, *J* = 4.7 Hz, -OCH_2-), 3.42 (4H, d, *J* = 13.4 Hz, -CH_2-), 4.13 (4H, t, *J* = 4.7 Hz, -$OCH_2C\boldsymbol{H_2}$-), 4.35 (4H, d, *J* = 13.4 Hz, -CH_2-), 6.42 (4H, d, *J* = 8.6 Hz, -C_6H_4-), 6.52 (2H, s, -OH), 7.04 (8H, s, -C_6H_2-), 7.16 (4H, d, *J* = 8.6 Hz, -C_6H_4-), 7.33 (6H, m, -C_6H_3-), 8.90 (2H, s, -NH). IR (KBr disk/cm^{-1}): 2215 *v*(N≡C). Positive-ion ESI-MS: m/z 1589 [M]$^+$. Elemental analysis, Anal. Found (%): C, 60.70; H, 5.75; N, 3.48. Calcd. For $C_{82}H_{90}Au_2N_4O_4{\cdot}2H_2O$: C, 60.59; H, 5.83; N, 3.45.

Computational Details

Geometry optimization was performed on **1** and the aluminum ion-bound complex (**1**·Al^{3+}) with C_2 and C_1 symmetry, respectively, using the simple local Xα exchange potential (Slater's exchange parameter α = 0.7)[2] with a pruned (99,590) grid. The Stuttgart effective core potentials (ECPs) and the associated basis set were applied to describe Au[3] with two f-type polarization functions (ζ = 0.200, 1.190).[4] For Al, O, N, C, and H atoms, the 6-31G basis set was used with d-type polarization functions for the Al (ζ = 0.325), O, N and the alkynyl, isocyanide and carbonyl carbons (ζ = 0.800) as well as p-type polarization functions for the phenolic and amide hydrogens (ζ =1.100).[5] Vibrational frequency calculations were performed for the optimized structures to verify that each was a minimum on the potential surface. All calculations were performed with the use of the Gaussian 03 package.[6]

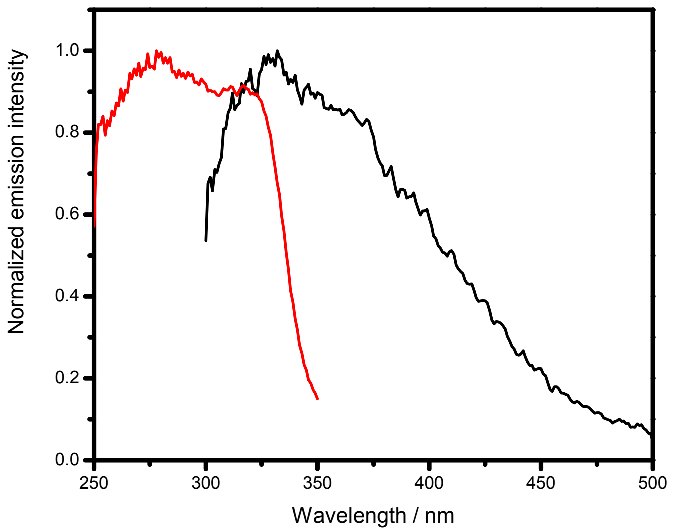


Fig S1 Excitation spectra of **1** (1.4 ×10^{-4} M) in the absence (——) and in the presence (——) of Al^{3+} (2.4 ×10^{-3} M) monitored at 450 and 640 nm, respectively

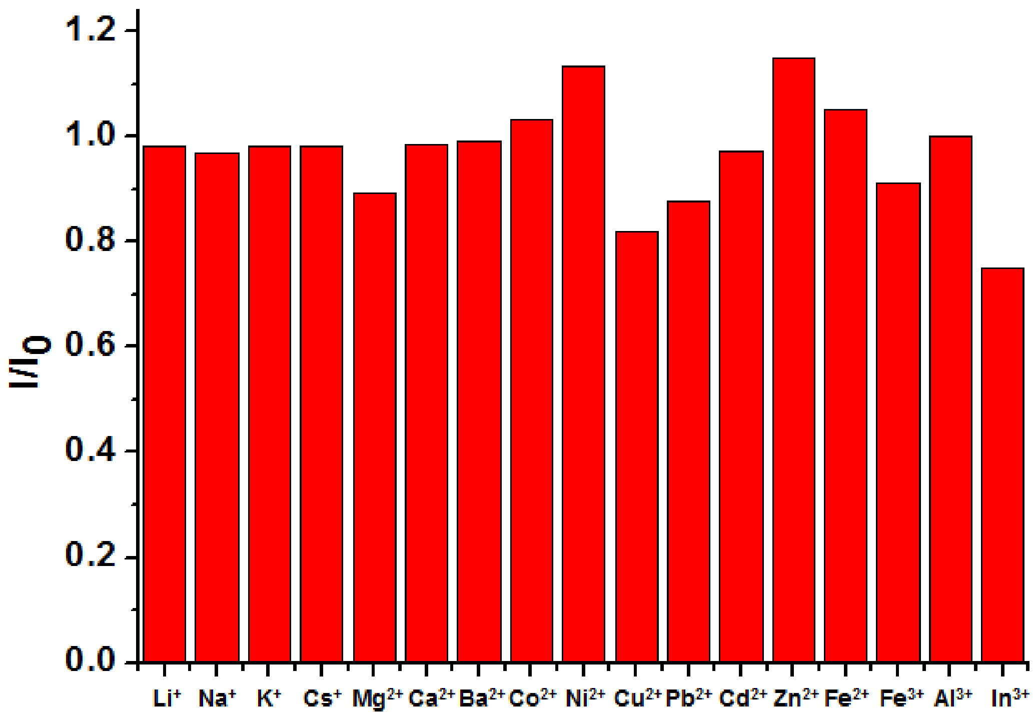


Fig S2 Responses of **1** (1 x 10^{-4} M) containing 3 equiv Al^{3+} in CH_2Cl_2-MeCN (1:1 v/v, 0.1M $^{n}Bu_4NPF_6$) upon addition of 3 equiv of different metal ions

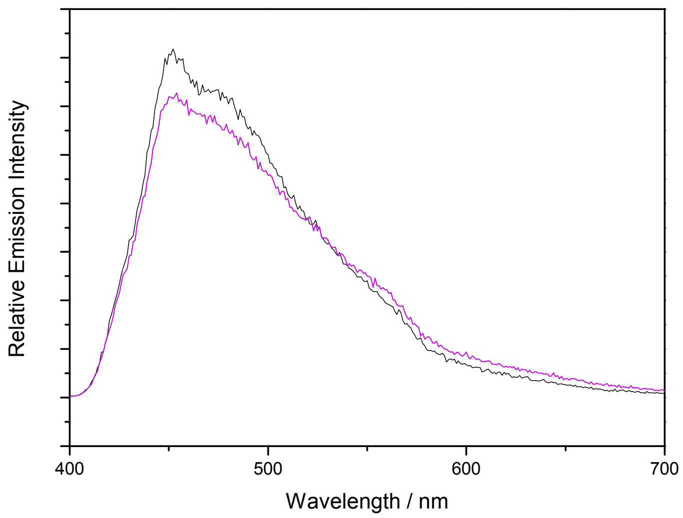


Fig S3 Emission spectral changes of **2** (1.5×10^{-5} M) in CH_2Cl_2-MeCN (1:1 v/v, containing 0.1 M $^{n}Bu_4NPF_6$) in the presence of a large excess of $Al(ClO_4)_3$

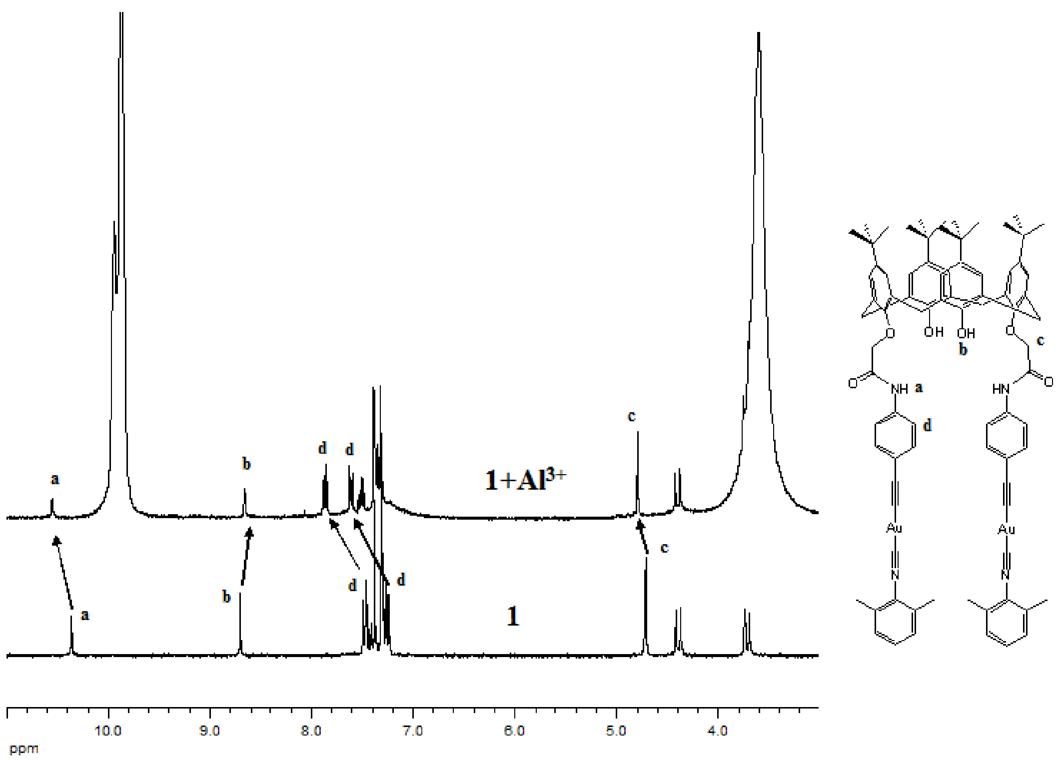


Fig S4 Partial ^{1}H NMR spectra (acetone-d_6) of **1** before (bottom) and after (top) addition of 20 equiv of $Al(ClO_4)_3$

Notes and references

1 X. He, W. H. Lam, N. Zhu and V. W.-W. Yam, *Chem. Eur. J.*, 2009, **15**, 8842.

2 (*a*) J. C. Slater, *Phys. Rev.*, 1951, **81**, 385; (*b*) K. Schwarz, *Phys. Rev. B*, 1972, **5**, 2466; (*c*) J. C. Slater, *Quantum Theory of Molecular and Solids, Vol. 4*, The Self-Consistent Field for Molecular and Solids McGraw-Hill, New York, 1974.

3 D. Andrae, U. Häussermann, M. Dolg, H. Stoll and H. Preuss, *Theor. Chim. Acta*, 1990, **77**, 123.

4 P. Pyykkö, N. Runeberg and F. Mendizabal, *Chem. Eur. J.*, 1997, **3**, 1451.

5 (*a*) R. Ditchfield, W. J. Hehre and J. A. Pople, *J. Chem. Phys.*, 1971, **54**, 724; (*b*) W. J. Hehre, R. Ditchfield and J. A. Pople, *J. Chem. Phys.*, 1972, **56**, 2257; (*c*) P. C. Hariharan and J. A. Pople, *Theor. Chim. Acta*, 1973, **28**, 213; (*d*) M. M. Francl, W. J. Pietro, W. J. Hehre, J. S. Binkley, M. S. Gordon, D. J. DeFrees and J. A. Pople, *J. Chem. Phys.*, 1982, **77**, 3654.

6. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez and J. A. Pople, *Gaussian 03 (Revision E.01)*, Gaussian, Inc., Wallingford CT, 2004.

Cartesian coordinates for the optimized geometries

1

1	C	2.883523	3.197282	-6.010221
2	C	2.516685	2.246521	-5.047664
3	C	1.242774	2.328990	-4.457975
4	C	0.358857	3.357155	-4.839585
5	C	0.770884	4.291862	-5.788723
6	C	2.031912	4.234790	-6.400994
7	C	3.452502	1.112092	-4.717471
8	C	3.017085	-0.191591	-5.344975
9	C	2.337287	-1.155557	-4.587056
10	C	1.871091	-2.348760	-5.142614
11	C	2.079506	-2.553696	-6.512989
12	C	2.721596	-1.606749	-7.317969
13	C	3.194868	-0.433560	-6.707869
14	C	1.061378	-3.343076	-4.341942
15	C	-0.358857	-3.357155	-4.839585
16	C	-1.242774	-2.328990	-4.457975
17	C	-2.516685	-2.246521	-5.047664
18	C	-2.883523	-3.197282	-6.010221
19	C	-2.031912	-4.234790	-6.400994
20	C	-0.770884	-4.291862	-5.788723
21	C	-3.452502	-1.112092	-4.717471
22	C	-3.017085	0.191591	-5.344975
23	C	-2.337287	1.155557	-4.587056
24	C	-1.871091	2.348760	-5.142614
25	C	-2.079506	2.553696	-6.512989
26	C	-2.721596	1.606749	-7.317969
27	C	-3.194868	0.433560	-6.707869
28	O	-2.031912	0.847732	-3.258844
29	C	-2.953247	1.335559	-2.262887
30	C	-2.252274	1.538103	-0.933475
31	N	-0.896517	1.583010	-1.018000
32	C	-0.000788	1.636163	0.057941
33	C	-0.421219	1.704910	1.397744
34	C	0.526192	1.695890	2.413635
35	C	1.908261	1.615190	2.133854
36	C	2.313263	1.557997	0.780493
37	C	1.373688	1.579692	-0.238672
38	C	2.862308	1.591637	3.175118
39	C	3.700900	1.570311	4.084953
40	C	-2.868540	1.785080	-8.827104
41	C	-1.061378	3.343076	-4.341942
42	O	-0.794543	-1.449100	-3.511448
43	C	-2.400186	-5.256081	-7.473117
44	O	2.031912	-0.847732	-3.258844
45	C	2.953247	-1.335559	-2.262887
46	C	2.252274	-1.538103	-0.933475
47	N	0.896517	-1.583010	-1.018000
48	C	0.000788	-1.636163	0.057941
49	C	-1.373688	-1.579692	-0.238672
50	C	-2.313263	-1.557997	0.780493
51	C	-1.908261	-1.615190	2.133854
52	C	-0.526192	-1.695890	2.413635
53	C	0.421219	-1.704910	1.397744
54	C	-2.862308	-1.591637	3.175118
55	C	-3.700900	-1.570311	4.084953
56	C	2.868540	-1.785080	-8.827104
57	O	0.794543	1.449100	-3.511448
58	C	2.400186	5.256081	-7.473117
59	O	-2.938949	1.660863	0.075070
60	O	2.938949	-1.660863	0.075070
61	H	-1.495689	1.743118	1.613001
62	H	0.201075	1.737583	3.462700
63	H	3.385317	1.486372	0.551035
64	H	1.687314	1.552922	-1.294888
65	H	-1.687314	-1.552922	-1.294888
66	H	-3.385317	-1.486372	0.551035
67	H	-0.201075	-1.737583	3.462700
68	H	1.495689	-1.743118	1.613001
69	H	-3.692352	-0.340924	-7.315138
70	H	-1.670500	3.470271	-6.963101
71	H	-4.465699	-1.374417	-5.087920
72	H	-3.542990	-0.988297	-3.614917
73	H	-0.063538	-5.090578	-6.070098
74	H	-3.883972	-3.109150	-6.460954
75	H	1.496776	-4.358601	-4.459995
76	H	1.098342	-3.089712	-3.262785
77	H	3.692352	0.340924	-7.315138
78	H	1.670500	-3.470271	-6.963101
79	H	3.542990	0.988297	-3.614917
80	H	4.465699	1.374417	-5.087920
81	H	0.063538	5.090578	-6.070098
82	H	3.883972	3.109150	-6.460954
83	H	-1.098342	3.089712	-3.262785
84	H	-1.496776	4.358601	-4.459995
85	H	-3.791353	0.620814	-2.102023
86	H	-3.386635	2.299383	-2.611925
87	H	3.791353	-0.620814	-2.102023
88	H	3.386635	-2.299383	-2.611925
89	H	0.479163	-1.486120	-1.965769
90	H	-0.479163	1.486120	-1.965769
91	H	-1.372498	-0.630313	-3.402846
92	H	1.372498	0.630313	-3.402846
93	C	2.317940	6.674341	-6.888346
94	H	2.555049	7.426658	-7.670985
95	H	1.303097	6.895238	-6.497235
96	H	3.038454	6.798428	-6.053502
97	C	3.812465	5.034660	-8.014271
98	H	4.574937	5.125634	-7.211905
99	H	3.916818	4.034183	-8.485730
100	H	4.039552	5.798362	-8.787016
101	C	1.407126	5.132834	-8.641836
102	H	1.454047	4.117799	-9.090905
103	H	0.362556	5.309653	-8.307846
104	H	1.645672	5.877485	-9.431539
105	C	-2.305516	3.123622	-9.306986
106	H	-2.831974	3.980756	-8.835647
107	H	-1.219317	3.217254	-9.089248
108	H	-2.438049	3.207814	-10.405737
109	C	-2.103142	0.652747	-9.534217
110	H	-2.485646	-0.345554	-9.235179
111	H	-2.211141	0.749533	-10.635831
112	H	-1.021243	0.691014	-9.283174
113	C	-4.353302	1.711025	-9.214510
114	H	-4.929276	2.527667	-8.731547
115	H	-4.465323	1.808479	-10.315452
116	H	-4.807063	0.745453	-8.908913
117	C	2.103142	-0.652747	-9.534217
118	H	1.021243	-0.691014	-9.283174
119	H	2.485646	0.345554	-9.235179
120	H	2.211141	-0.749533	-10.635831
121	C	2.305516	-3.123622	-9.306986
122	H	2.831974	-3.980756	-8.835647
123	H	1.219317	-3.217254	-9.089248
124	H	2.438049	-3.207814	-10.405737
125	C	4.353302	-1.711025	-9.214510
126	H	4.929276	-2.527667	-8.731547
127	H	4.465323	-1.808479	-10.315452
128	H	4.807063	-0.745453	-8.908913
129	C	-1.407126	-5.132834	-8.641836
130	H	-1.454047	-4.117799	-9.090905
131	H	-0.362556	-5.309653	-8.307846
132	H	-1.645672	-5.877485	-9.431539
133	C	-3.812465	-5.034660	-8.014271
134	H	-4.574937	-5.125634	-7.211905
135	H	-3.916818	-4.034183	-8.485730
136	H	-4.039552	-5.798362	-8.787016
137	C	-2.317940	-6.674341	-6.888346
138	H	-3.038454	-6.798428	-6.053502
139	H	-2.555049	-7.426658	-7.670985
140	H	-1.303097	-6.895238	-6.497235
141	Au	-5.009351	-1.523938	5.506419
142	Au	5.009351	1.523938	5.506419
143	C	-6.302474	-1.472435	6.915760
144	C	6.302474	1.472435	6.915760
145	N	-7.099696	-1.437084	7.788164
146	N	7.099696	1.437084	7.788164
147	C	-8.019026	-1.395816	8.799190
148	C	-7.571075	-1.575469	10.126986
149	C	-9.375166	-1.175040	8.470591
150	C	-8.531666	-1.528505	11.140921
151	C	-10.293470	-1.137577	9.523332
152	C	-9.879572	-1.312106	10.845838
153	H	-11.354859	-0.966811	9.290938
154	C	8.019026	1.395816	8.799190
155	C	7.571075	1.575469	10.126986
156	C	9.375166	1.175040	8.470591
157	C	8.531666	1.528505	11.140921
158	C	10.293470	1.137577	9.523332
159	C	9.879572	1.312106	10.845838
160	H	11.354859	0.966811	9.290938
161	H	8.205649	1.665723	12.182361
162	H	-8.205649	-1.665723	12.182361
163	H	-10.618583	-1.278782	11.658789
164	H	10.618583	1.278782	11.658789
165	C	9.782297	0.991774	7.046785
166	H	9.269069	0.122619	6.581286
167	H	9.517767	1.875467	6.426583
168	H	10.873578	0.829468	6.962680
169	C	6.123290	1.804238	10.406363
170	H	5.743676	2.712955	9.890945
171	H	5.496617	0.959992	10.045695
172	H	5.941593	1.925529	11.491059
173	C	-6.123290	-1.804238	10.406363
174	H	-5.743676	-2.712955	9.890945
175	H	-5.496617	-0.959992	10.045695
176	H	-5.941593	-1.925529	11.491059
177	C	-9.782297	-0.991774	7.046785
178	H	-9.269069	-0.122619	6.581286
179	H	-9.517767	-1.875467	6.426583
180	H	-10.873578	-0.829468	6.962680

1·Al^{3+}

1	C	-2.680836	-2.212965	-0.246100
2	C	-1.585081	-1.811588	-1.057231
3	C	-0.274966	-1.997882	-0.647863
4	C	-0.024716	-2.611302	0.593605
5	C	-1.093252	-3.076791	1.384854
6	C	-2.398801	-2.880724	0.975819
7	N	1.262068	-2.779345	1.134526
8	C	2.427629	-2.261893	0.803377
9	C	3.641520	-2.581373	1.622184
10	O	4.663490	-1.682746	1.126270
11	C	5.973261	-2.115395	1.521129
12	C	6.485366	-1.658759	2.733303
13	C	7.753390	-2.119158	3.110596
14	C	8.477663	-3.026114	2.325290
15	C	7.884470	-3.488036	1.137074
16	C	6.626287	-3.054739	0.715220
17	C	5.754084	-0.632661	3.560295
18	C	6.233395	0.743805	3.192211
19	C	5.700335	1.452887	2.114023
20	C	6.191091	2.695326	1.709532
21	C	7.274020	3.227587	2.422510
22	C	7.858818	2.557406	3.503450
23	C	7.315239	1.315477	3.866375
24	O	4.527815	0.916957	1.445137
25	C	5.650602	3.439644	0.515513
26	C	6.344199	3.024962	-0.759269
27	C	5.836871	2.022232	-1.586660
28	C	6.438100	1.639270	-2.787557
29	C	7.638772	2.265419	-3.127630
30	C	8.223454	3.254188	-2.316996
31	C	7.554144	3.619385	-1.140306
32	C	9.043091	3.121600	4.277404
33	C	9.501220	4.469260	3.720544
34	C	9.866588	-3.517382	2.712709
35	C	9.835024	-5.046930	2.874863
36	C	6.041282	-3.545920	-0.587204
37	C	6.562289	-2.744870	-1.752285
38	C	5.960303	-1.557823	-2.184800
39	C	6.478521	-0.783206	-3.219124
40	C	7.670873	-1.215699	-3.816740
41	C	8.323753	-2.388885	-3.423264
42	C	7.738452	-3.140686	-2.392366
43	O	4.697579	-1.166564	-1.582663
44	C	9.624747	-2.860239	-4.059218
45	C	9.402327	-4.242392	-4.696956
46	C	5.867792	0.527663	-3.630448
47	O	4.572563	1.440999	-1.238881
48	C	3.462033	2.184916	-1.804718
49	C	2.322153	1.934541	-0.870163
50	N	1.207095	2.629933	-0.981868
51	C	-0.068396	2.438152	-0.422351
52	C	-1.033919	3.422540	-0.710156
53	C	-2.344853	3.250232	-0.306846
54	C	-2.737354	2.077572	0.391070
55	C	-1.735836	1.120684	0.707904
56	C	-0.420766	1.290917	0.311786
57	C	9.541517	3.890939	-2.739148
58	C	10.024588	4.933255	-1.730860
59	C	10.214441	2.126871	4.188031
60	C	8.640796	3.303490	5.751084
61	C	10.351129	-2.892179	4.020837
62	C	10.853990	-3.143582	1.592276
63	C	10.700925	-2.970813	-2.964000
64	C	10.118661	-1.892741	-5.134501
65	C	10.608873	2.788275	-2.859378
66	C	9.357437	4.571726	-4.106538
67	O	2.610174	-1.462800	-0.194947
68	O	2.481306	0.960554	-0.035943
69	Al	3.990401	-0.162390	-0.085199
70	H	7.666163	4.209074	2.118850
71	H	7.743771	0.767915	4.720521
72	H	5.954217	-0.814064	4.635433
73	H	4.655497	-0.708494	3.414929
74	H	8.185382	-1.755180	4.053923
75	H	8.425224	-4.218424	0.514693
76	H	4.927382	-3.536397	-0.548588
77	H	6.326000	-4.608068	-0.732718
78	H	8.217870	-4.078439	-2.069925
79	H	8.093468	-0.608729	-4.630361
80	H	4.761704	0.480506	-3.540554
81	H	6.097810	0.718311	-4.697990
82	H	8.135476	1.974855	-4.066751
83	H	7.980163	4.403517	-0.497765
84	H	4.547541	3.307442	0.418964
85	H	5.811679	4.525376	0.675626
86	H	9.950638	1.133369	4.609480
87	H	11.076557	2.516264	4.767415
88	H	10.542054	1.984031	3.137282
89	H	8.334686	2.345574	6.220989
90	H	7.803511	4.023665	5.855172
91	H	9.504132	3.696642	6.326145
92	H	10.368215	4.834053	4.306823
93	H	8.707292	5.242373	3.796286
94	H	9.829698	4.392068	2.661342
95	H	9.698780	-3.162433	4.878218
96	H	10.417468	-1.784301	3.953056
97	H	11.367490	-3.268075	4.253652
98	H	10.917458	-2.043159	1.462990
99	H	10.569473	-3.591364	0.615979
100	H	11.865539	-3.518972	1.850092
101	H	9.139694	-5.353291	3.683122
102	H	10.848299	-5.413331	3.138630
103	H	9.527994	-5.559691	1.939411
104	H	11.649619	-3.331945	-3.411366
105	H	10.413290	-3.690004	-2.167291
106	H	10.895948	-1.986359	-2.489940
107	H	11.070645	-2.269211	-5.559311
108	H	10.320258	-0.880250	-4.721439
109	H	9.398830	-1.802240	-5.975502
110	H	10.351069	-4.602232	-5.145295
111	H	8.638941	-4.198236	-5.500546
112	H	9.077443	-4.997835	-3.951226
113	H	10.781136	2.286715	-1.884531
114	H	11.568236	3.236126	-3.190490
115	H	10.326383	2.014020	-3.604210
116	H	10.318467	5.022067	-4.429320
117	H	8.600531	5.381204	-4.056183
118	H	9.045383	3.852676	-4.892422
119	H	10.199060	4.491389	-0.725958
120	H	9.312045	5.779789	-1.633516
121	H	10.989153	5.357541	-2.074486
122	H	3.499506	-2.419087	2.715757
123	H	4.000721	-3.626014	1.473050
124	H	3.262064	1.807936	-2.836262
125	H	3.753525	3.255645	-1.879818
126	H	3.812800	1.599296	1.465490
127	H	4.081608	-1.941532	-1.599707
128	H	1.247697	3.421593	-1.641056
129	H	1.273508	-3.382330	1.971132
130	H	-0.751913	4.326944	-1.274858
131	H	0.323853	0.515994	0.529091
132	H	-3.105410	4.005581	-0.544024
133	H	-2.034368	0.212467	1.249894
134	H	0.556419	-1.663500	-1.279851
135	H	-0.893308	-3.581850	2.344764
136	H	-1.800404	-1.325103	-2.017919
137	H	-3.236995	-3.222496	1.597159
138	C	-4.077763	1.831072	0.713618
139	C	-5.257953	1.537684	0.951685
140	C	-3.999883	-1.912422	-0.607663
141	C	-5.167141	-1.583698	-0.863743
142	Au	-6.961365	-0.925163	-1.202401
143	Au	-7.072058	0.914380	1.242513
144	C	-8.737954	-0.229392	-1.559376
145	C	-8.863783	0.232020	1.539147
146	N	-9.801343	0.265885	-1.643571
147	N	-9.931980	-0.259214	1.572718
148	C	-10.956357	1.001399	-1.639827
149	C	-10.834982	2.397903	-1.429895
150	C	-12.193151	0.345960	-1.828707
151	C	-12.018367	3.141466	-1.412453
152	C	-13.342393	1.142635	-1.799857
153	C	-13.258692	2.522378	-1.597750
154	H	-11.958686	4.228210	-1.257094
155	H	-14.320151	0.662995	-1.950023
156	H	-14.175530	3.128206	-1.588190
157	C	-11.088917	-0.988352	1.513647
158	C	-10.965914	-2.386524	1.316243
159	C	-12.329663	-0.323857	1.633462
160	C	-12.151600	-3.122329	1.238124
161	C	-13.481063	-1.112722	1.545134
162	C	-13.395827	-2.493934	1.353107
163	H	-12.091313	-4.210091	1.090389
164	H	-14.462281	-0.626127	1.640117
165	H	-14.314968	-3.093614	1.295823
166	C	-9.493416	3.024809	-1.244187
167	H	-8.929723	2.572923	-0.394067
168	H	-8.851970	2.896949	-2.143926
169	H	-9.587852	4.109615	-1.048988
170	C	-12.253698	-1.130624	-2.025733
171	H	-11.540974	-1.476519	-2.804084
172	H	-12.002532	-1.677981	-1.088414
173	H	-13.268742	-1.448153	-2.330075
174	C	-12.388747	1.153619	1.823270
175	H	-11.737693	1.491982	2.657160
176	H	-12.054873	1.696541	0.909620
177	H	-13.421241	1.483618	2.044036
178	C	-9.620448	-3.022434	1.203153
179	H	-9.011563	-2.578440	0.381105
180	H	-9.025767	-2.893813	2.134306
181	H	-9.711444	-4.107667	1.008872