Supporting Information for:

On the Nature of Inter-Anion Coinage Bonds

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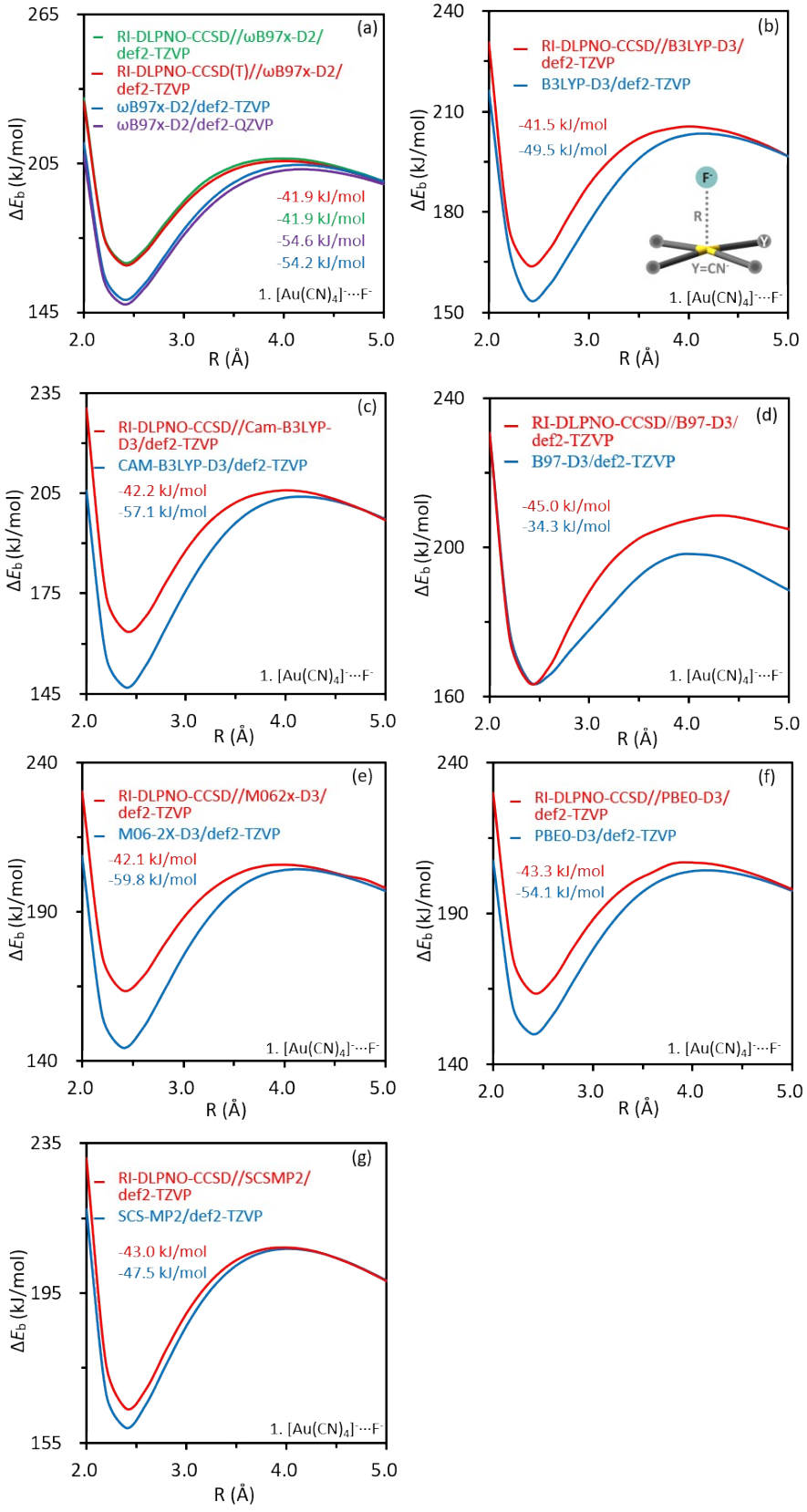
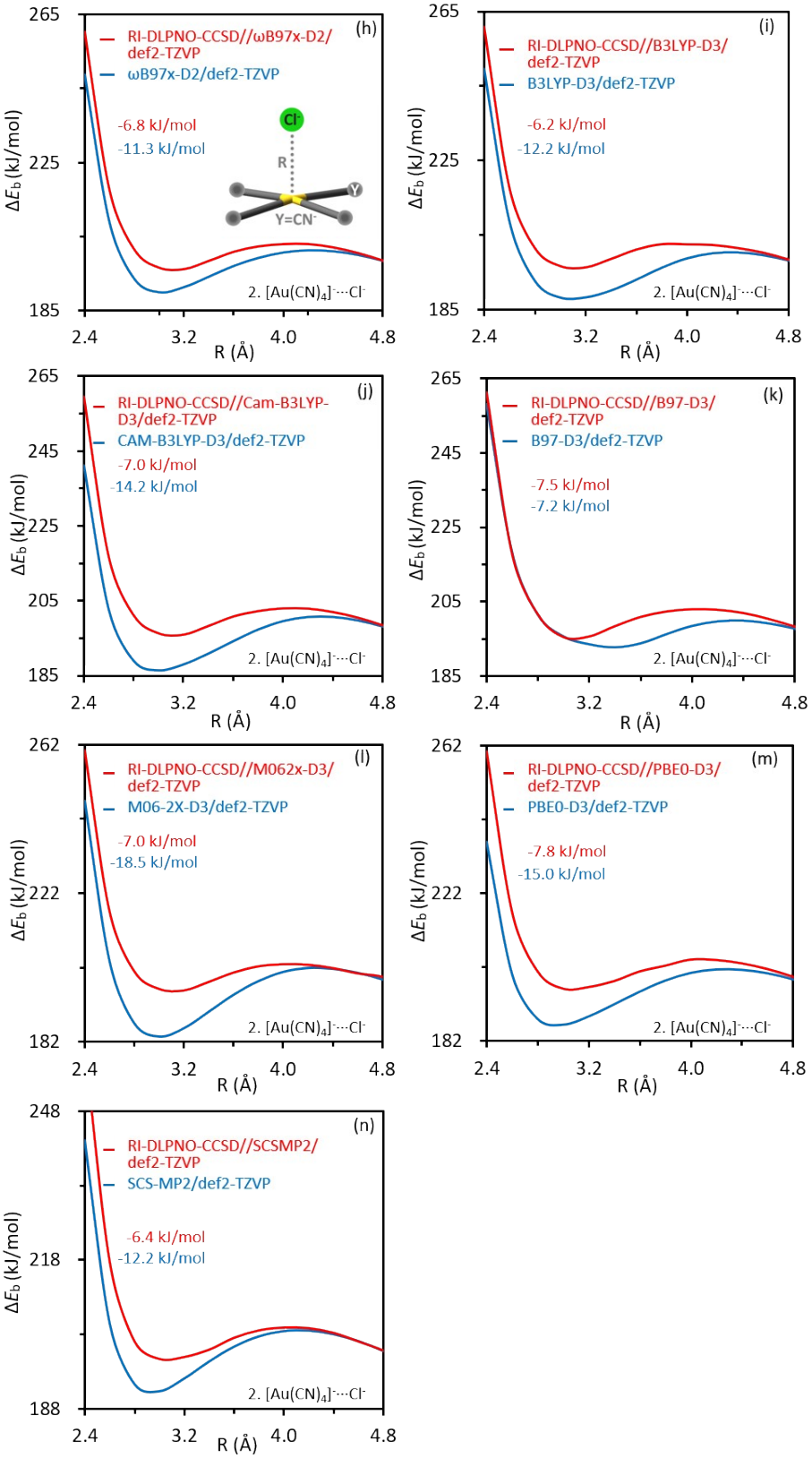
Additional Figures

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ωB97x-D2/def2-TZVP
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-11.3 kJ/mol
Cl⁻
R
Y
Y=CN⁻
2. [Au(CN)4]⁻···Cl⁻
ΔEb (kJ/mol)
R (Å)
(i)
RI-DLPNO-CCSD//B3LYP-D3/def2-TZVP
B3LYP-D3/def2-TZVP
-6.2 kJ/mol
-12.2 kJ/mol
(j)
RI-DLPNO-CCSD//Cam-B3LYP-D3/def2-TZVP
CAM-B3LYP-D3/def2-TZVP
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-14.2 kJ/mol
(k)
RI-DLPNO-CCSD//B97-D3/def2-TZVP
B97-D3/def2-TZVP
-7.5 kJ/mol
-7.2 kJ/mol
(l)
RI-DLPNO-CCSD//M062x-D3/def2-TZVP
M06-2X-D3/def2-TZVP
-7.0 kJ/mol
-18.5 kJ/mol
(m)
RI-DLPNO-CCSD//PBE0-D3/def2-TZVP
PBE0-D3/def2-TZVP
-7.8 kJ/mol
-15.0 kJ/mol
(n)
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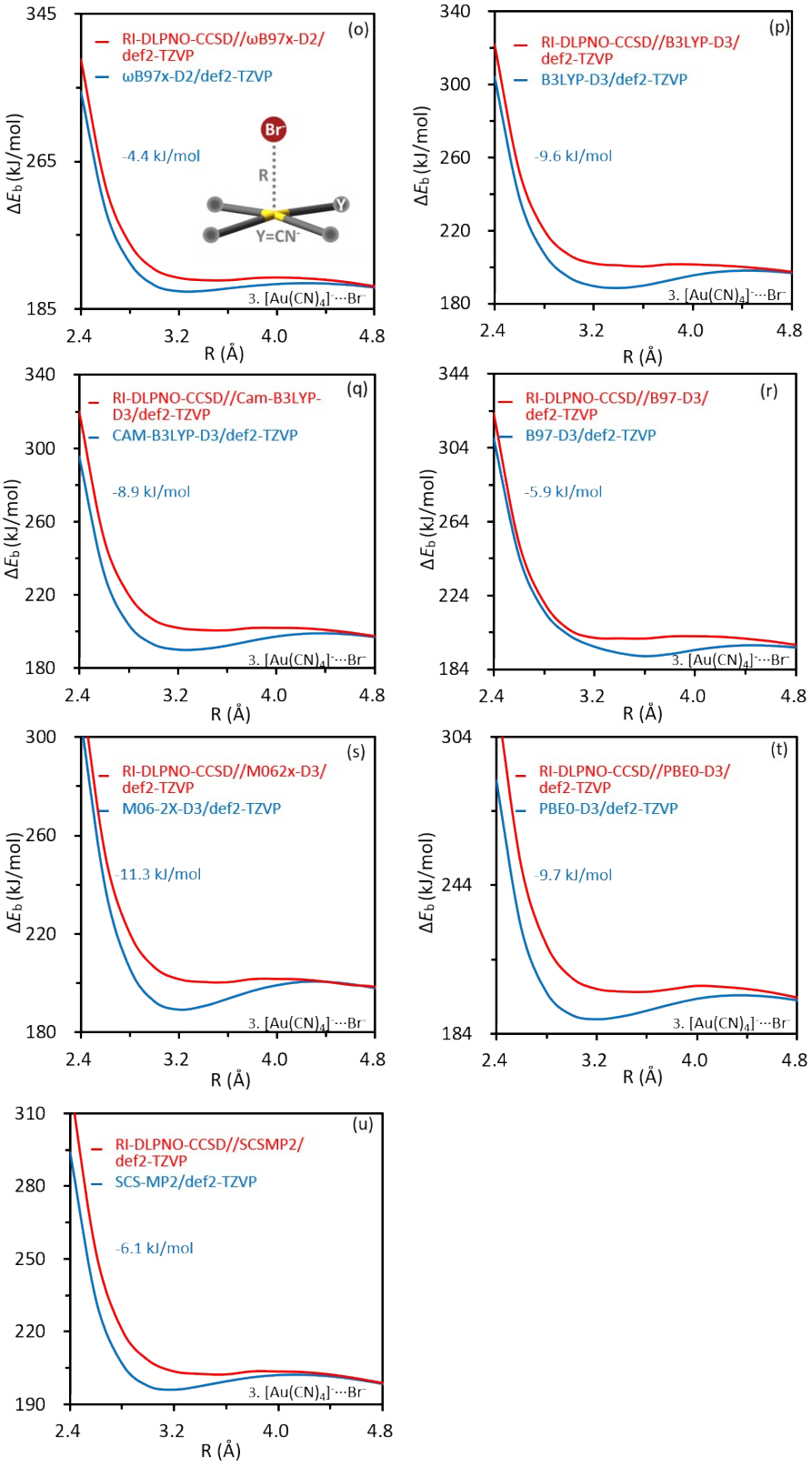
-12.2 kJ/mol


(o)
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ωB97x-D2/def2-TZVP
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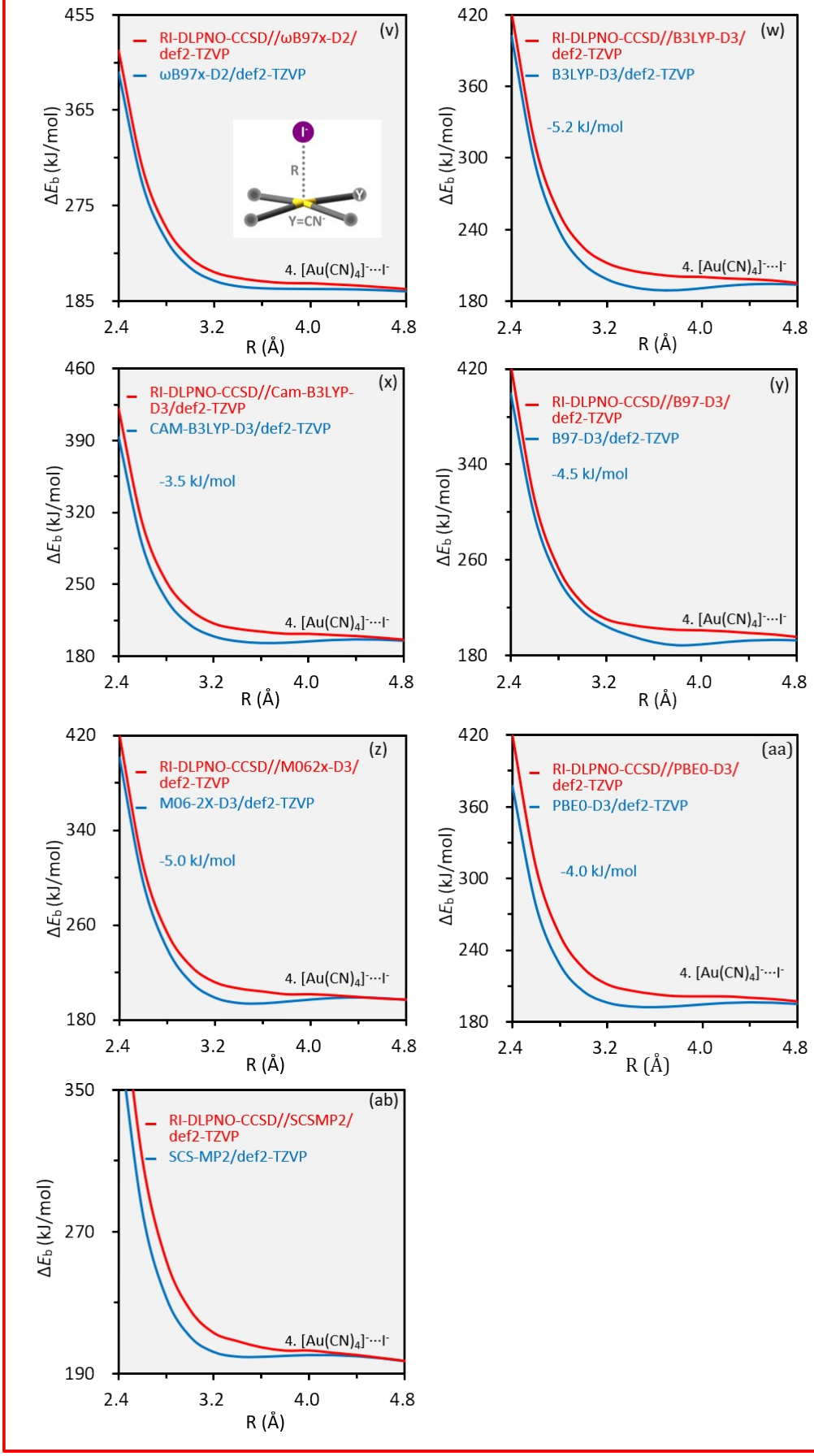
Br⁻
R
Y
Y=CN⁻
3. [Au(CN)4]⁻···Br⁻
ΔEb (kJ/mol)
R (Å)
(p)
RI-DLPNO-CCSD//B3LYP-D3/def2-TZVP
B3LYP-D3/def2-TZVP
-9.6 kJ/mol
(q)
RI-DLPNO-CCSD//Cam-B3LYP-D3/def2-TZVP
CAM-B3LYP-D3/def2-TZVP
-8.9 kJ/mol
(r)
RI-DLPNO-CCSD//B97-D3/def2-TZVP
B97-D3/def2-TZVP
-5.9 kJ/mol
(s)
RI-DLPNO-CCSD//M062x-D3/def2-TZVP
M06-2X-D3/def2-TZVP
-11.3 kJ/mol
(t)
RI-DLPNO-CCSD//PBE0-D3/def2-TZVP
PBE0-D3/def2-TZVP
-9.7 kJ/mol
(u)
RI-DLPNO-CCSD//SCSMP2/def2-TZVP
SCS-MP2/def2-TZVP
-6.1 kJ/mol


(v)
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ωB97x-D2/def2-TZVP
4. [Au(CN)4]-···I-
(w)
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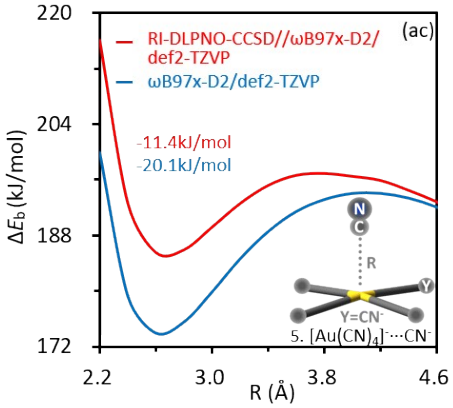
B3LYP-D3/def2-TZVP
-5.2 kJ/mol
(x)
RI-DLPNO-CCSD//Cam-B3LYP-D3/def2-TZVP
CAM-B3LYP-D3/def2-TZVP
-3.5 kJ/mol
(y)
RI-DLPNO-CCSD//B97-D3/def2-TZVP
B97-D3/def2-TZVP
-4.5 kJ/mol
(z)
RI-DLPNO-CCSD//M062x-D3/def2-TZVP
M06-2X-D3/def2-TZVP
-5.0 kJ/mol
(aa)
RI-DLPNO-CCSD//PBE0-D3/def2-TZVP
PBE0-D3/def2-TZVP
-4.0 kJ/mol
(ab)
RI-DLPNO-CCSD//SCSMP2/def2-TZVP
SCS-MP2/def2-TZVP
ΔEb (kJ/mol)
R (Å)
Y=CN-


(ac)
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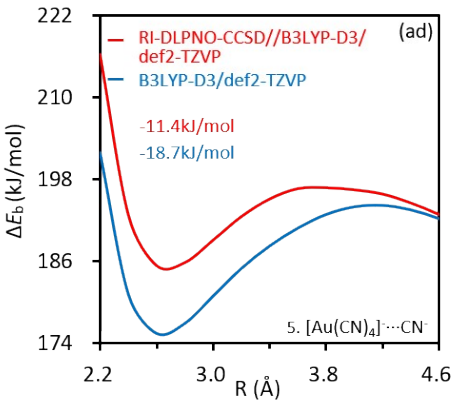
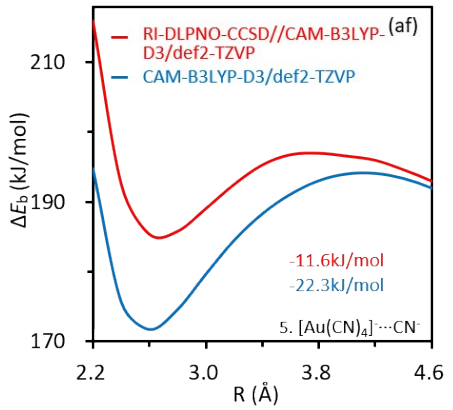
ωB97x-D2/def2-TZVP
-11.4kJ/mol
-20.1kJ/mol
N
C
R
Y
Y=CN⁻
5. [Au(CN)4]⁻···CN⁻
ΔEb (kJ/mol)
R (Å)
220
204
188
172
2.2
3.0
3.8
4.6


(ad)
RI-DLPNO-CCSD//B3LYP-D3/def2-TZVP
B3LYP-D3/def2-TZVP
-11.4kJ/mol
-18.7kJ/mol
5. [Au(CN)4]⁻···CN⁻
ΔEb (kJ/mol)
R (Å)
222
210
198
186
174
2.2
3.0
3.8
4.6


(af)
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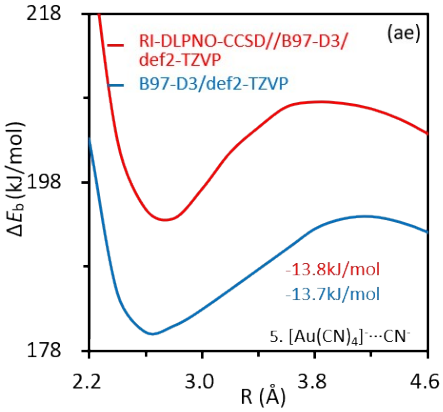
CAM-B3LYP-D3/def2-TZVP
-11.6kJ/mol
-22.3kJ/mol
5. [Au(CN)4]⁻···CN⁻
ΔEb (kJ/mol)
R (Å)
210
190
170
2.2
3.0
3.8
4.6


(ae)
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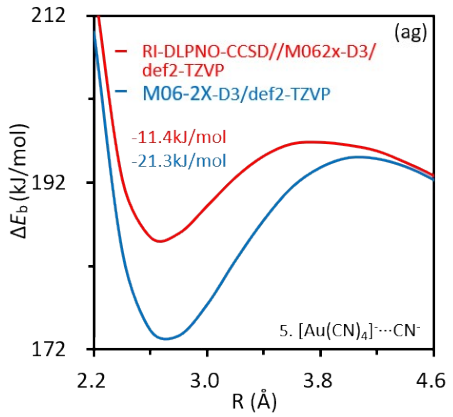
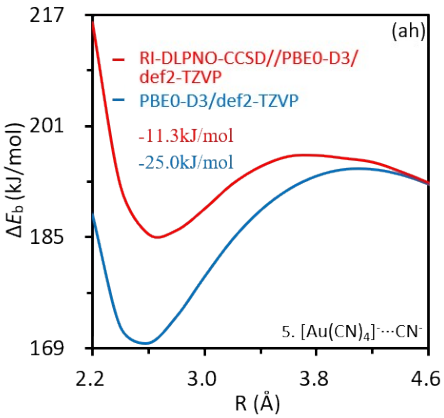
B97-D3/def2-TZVP
-13.8kJ/mol
-13.7kJ/mol
5. [Au(CN)4]⁻···CN⁻
ΔEb (kJ/mol)
R (Å)
218
198
178
2.2
3.0
3.8
4.6


(ag)
RI-DLPNO-CCSD//M062x-D3/def2-TZVP
M06-2X-D3/def2-TZVP
-11.4kJ/mol
-21.3kJ/mol
5. [Au(CN)4]⁻···CN⁻
ΔEb (kJ/mol)
R (Å)
212
192
172
2.2
3.0
3.8
4.6


(ah)
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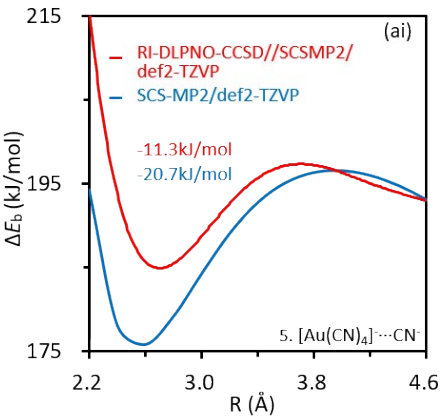
PBE0-D3/def2-TZVP
-11.3kJ/mol
-25.0kJ/mol
5. [Au(CN)4]⁻···CN⁻
ΔEb (kJ/mol)
R (Å)
217
201
185
169
2.2
3.0
3.8
4.6


(ai)
RI-DLPNO-CCSD//SCSMP2/def2-TZVP
SCS-MP2/def2-TZVP
-11.3kJ/mol
-20.7kJ/mol
5. [Au(CN)4]⁻···CN⁻
ΔEb (kJ/mol)
R (Å)
215
195
175
2.2
3.0
3.8
4.6

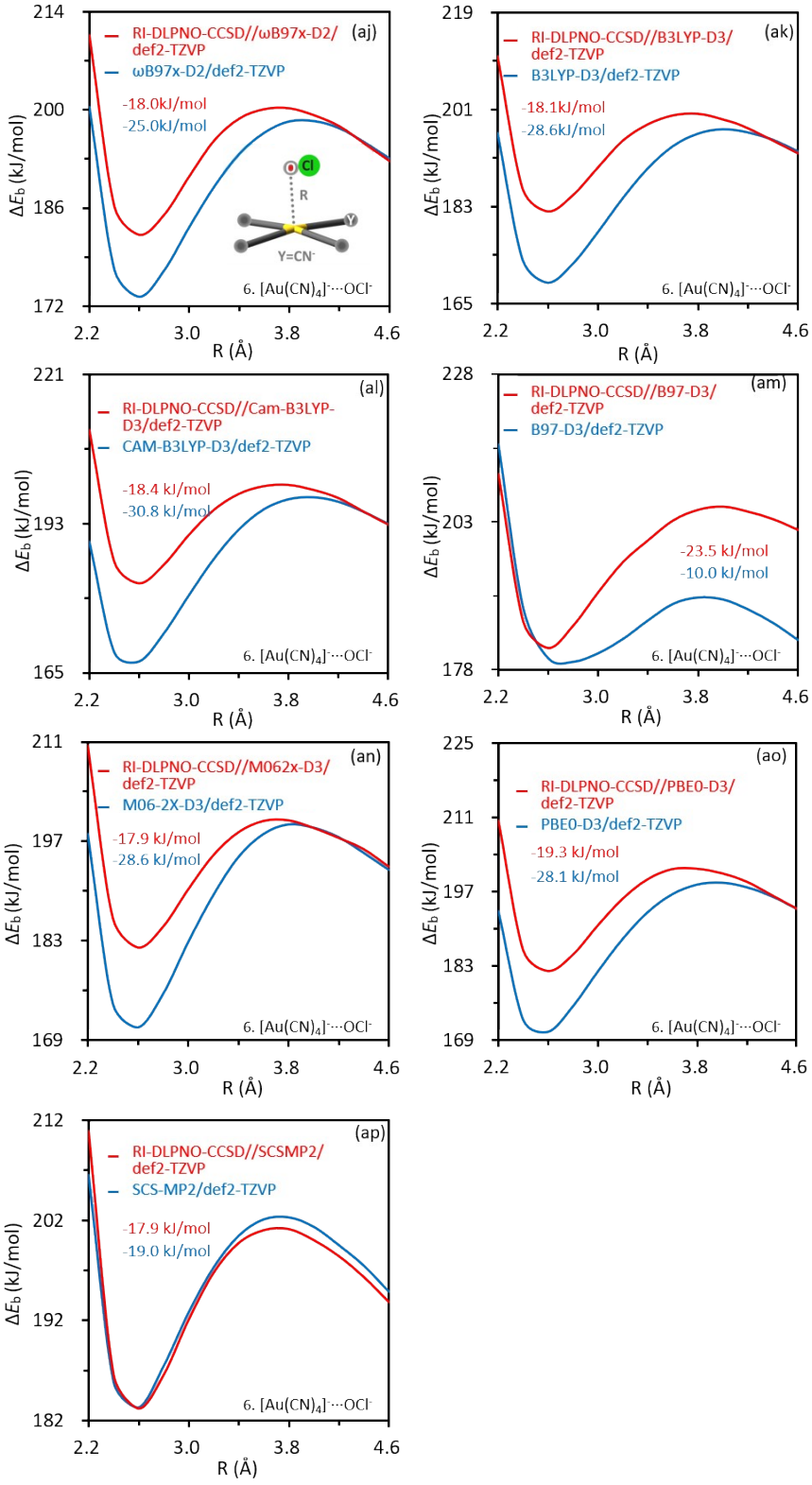
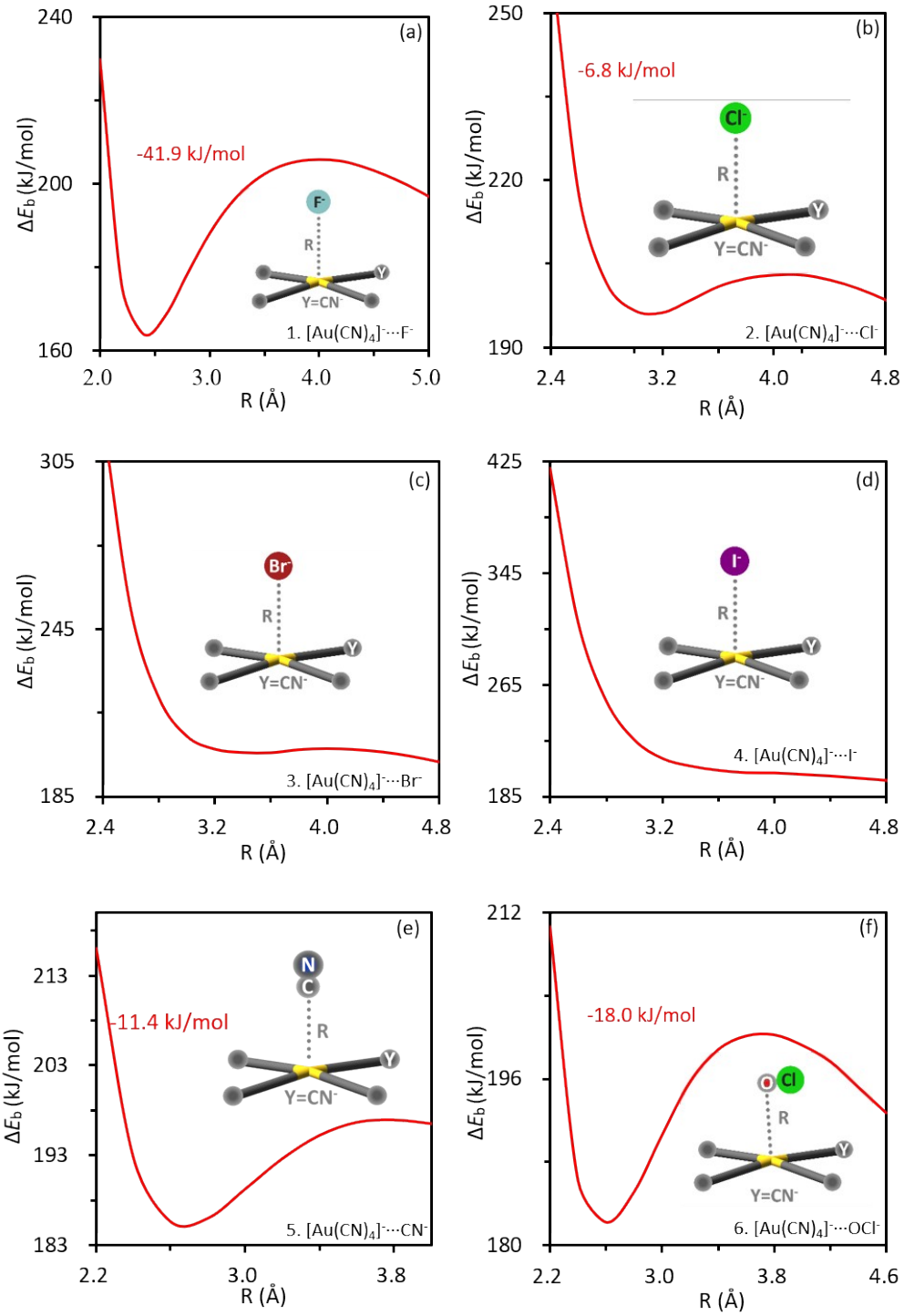
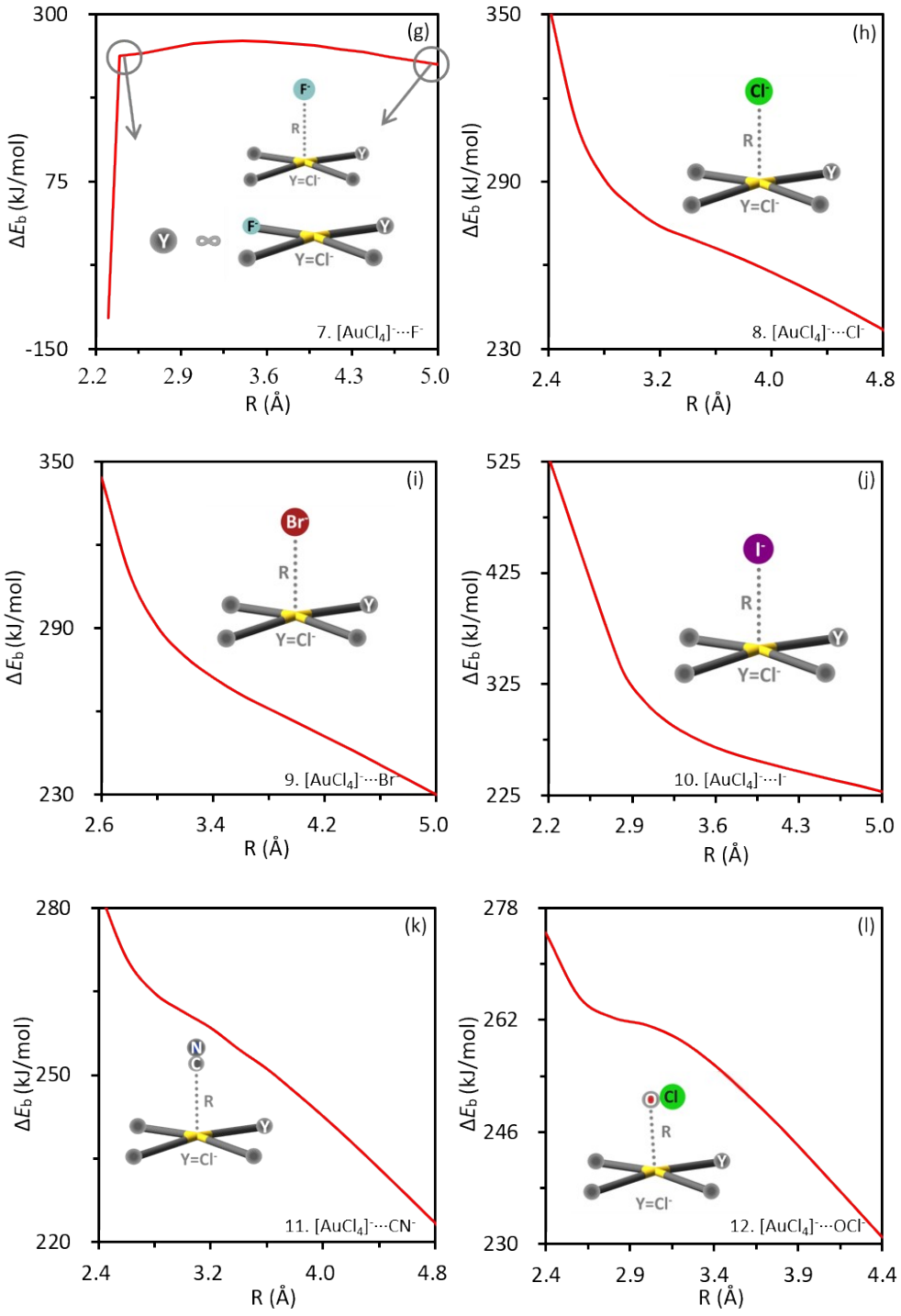
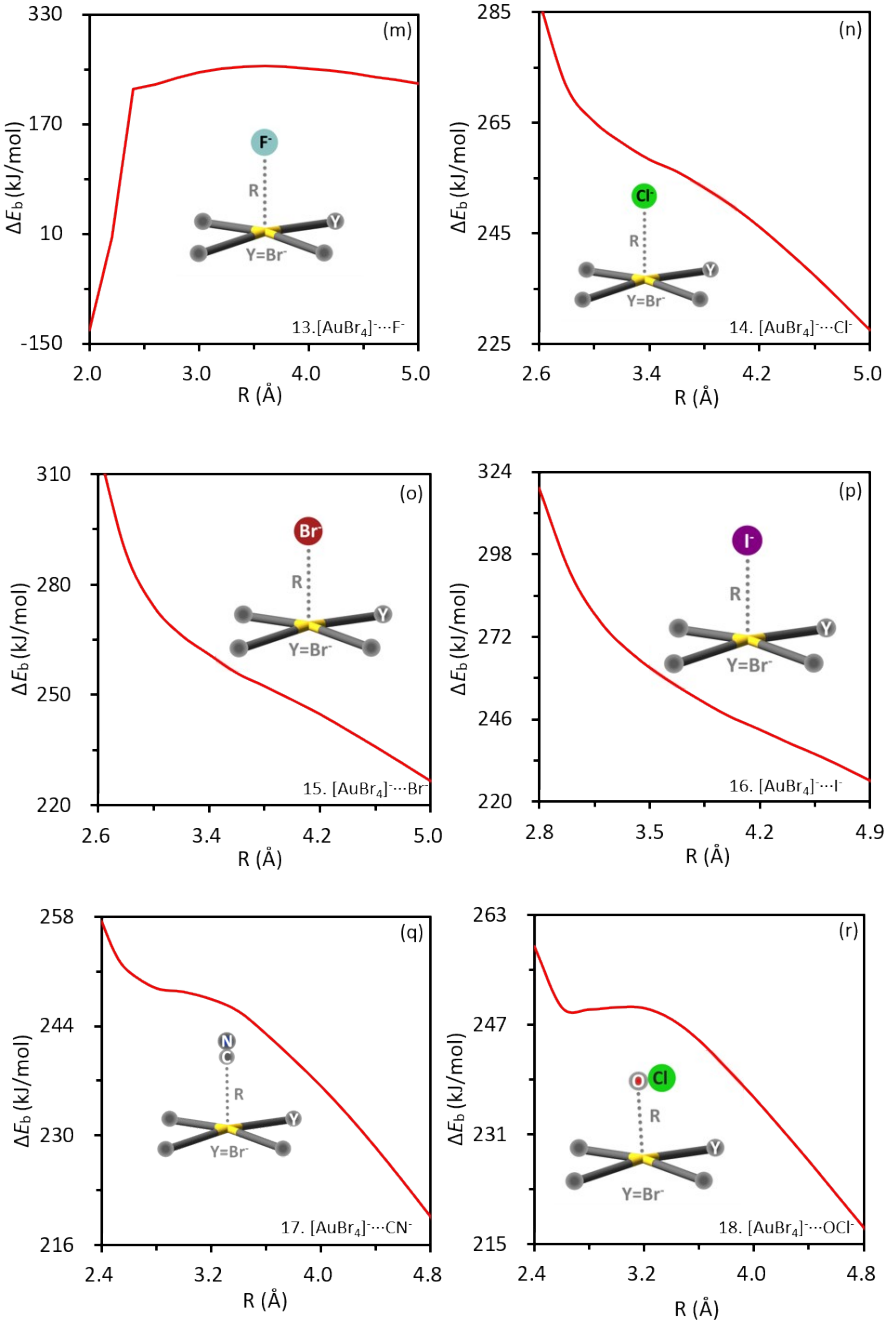
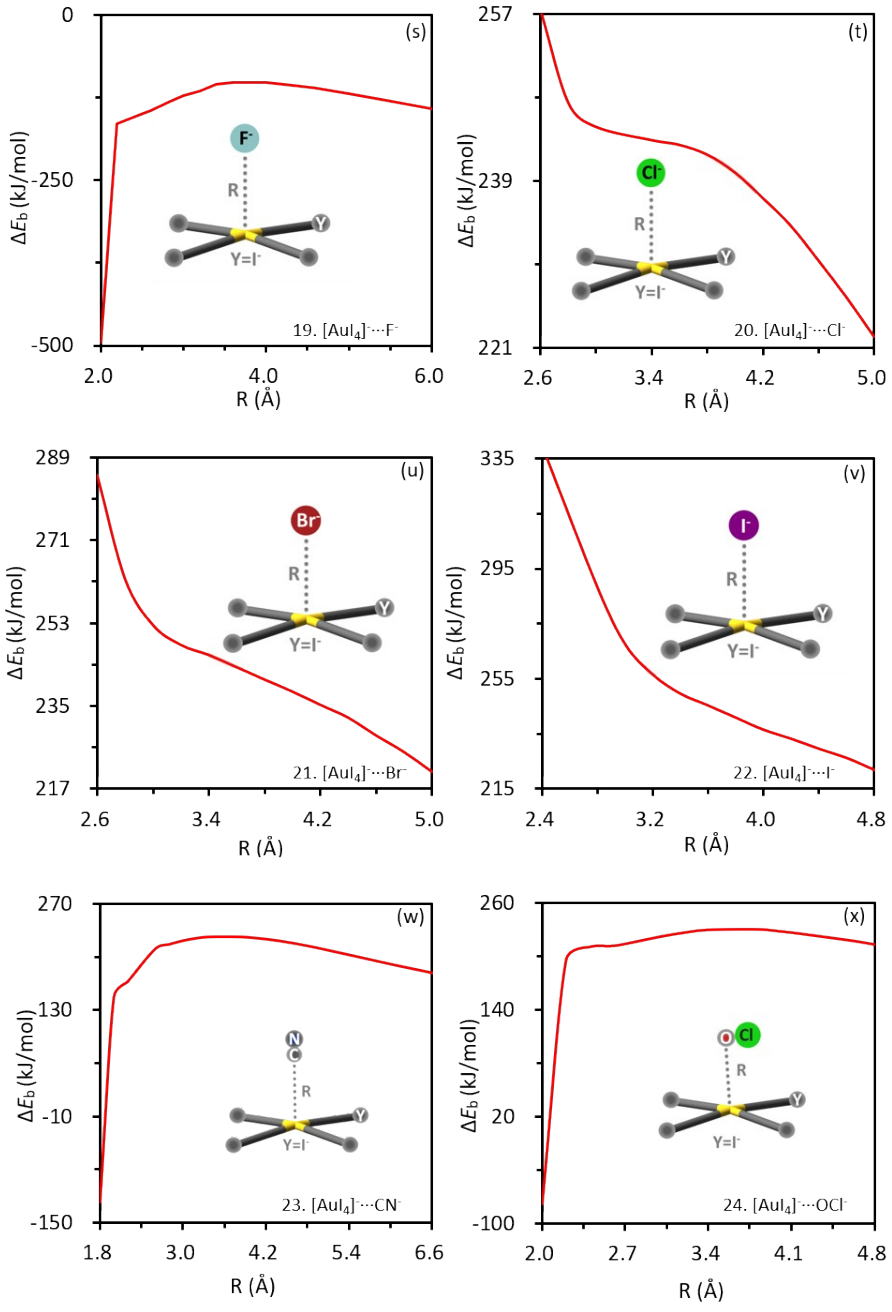


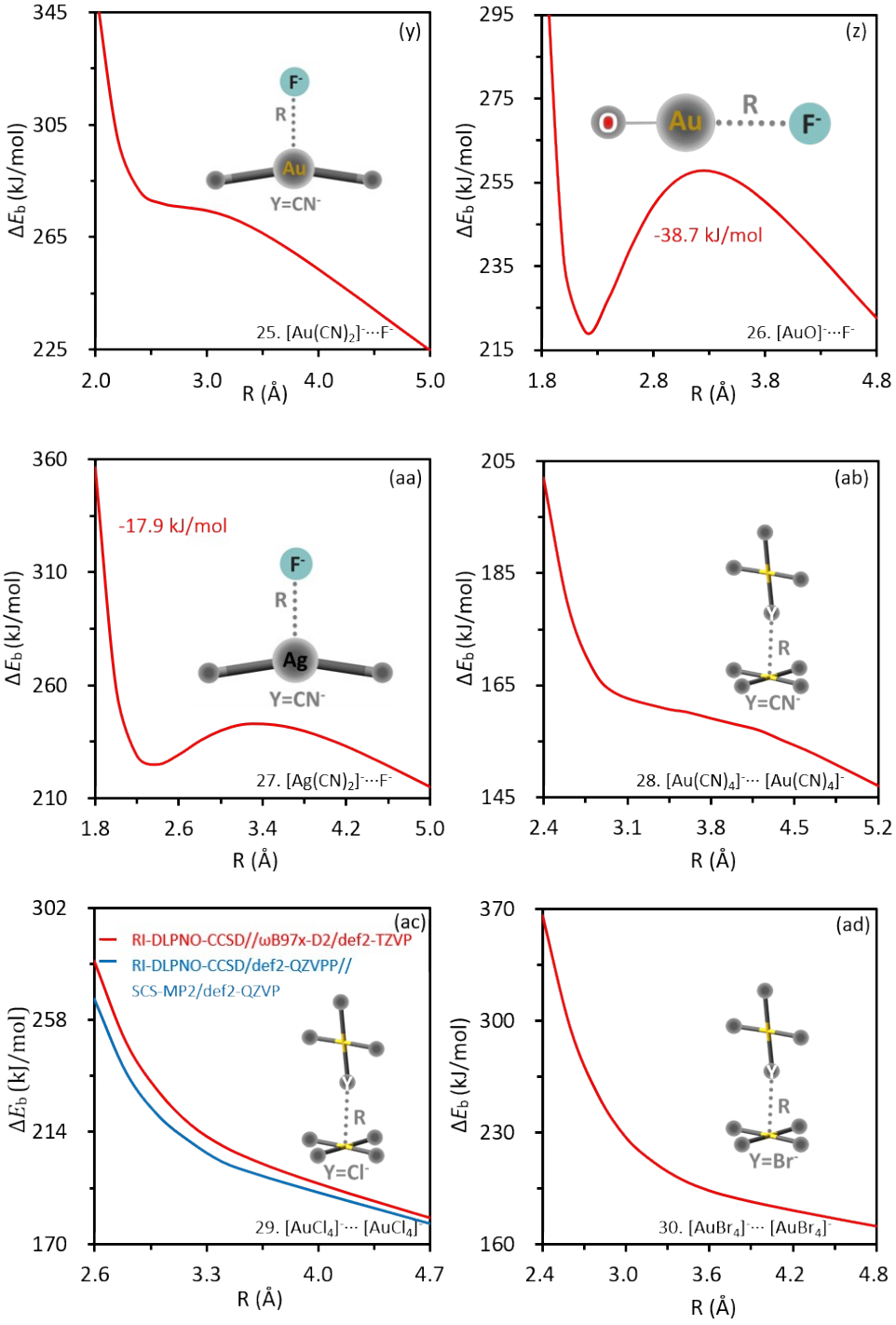
Fig. S1. Profiles of binding energy along the inter-anion distance for complexes **1-6** calculated at a series of theoretical levels.


(a)
-41.9 kJ/mol
F⁻
R
Y
Y=CN⁻
1. [Au(CN)4]⁻···F⁻
ΔEb (kJ/mol)
R (Å)
(b)
-6.8 kJ/mol
Cl⁻
2. [Au(CN)4]⁻···Cl⁻
(c)
Br⁻
3. [Au(CN)4]⁻···Br⁻
(d)
I⁻
4. [Au(CN)4]⁻···I⁻
(e)
N
C
-11.4 kJ/mol
5. [Au(CN)4]⁻···CN⁻
(f)
-18.0 kJ/mol
Cl
6. [Au(CN)4]⁻···OCl⁻


(g)
7. [AuCl4]-···F-
ΔEb (kJ/mol)
R (Å)
(h)
8. [AuCl4]-···Cl-
(i)
9. [AuCl4]-···Br-
(j)
10. [AuCl4]-···I-
(k)
11. [AuCl4]-···CN-
(l)
12. [AuCl4]-···OCl-
Y=Cl-


(m)
330
170
10
-150
ΔEb (kJ/mol)
2.0
3.0
4.0
5.0
R (Å)
F-
R
Y
Y=Br-
13.[AuBr4]-···F-
(n)
285
265
245
225
ΔEb (kJ/mol)
2.6
3.4
4.2
5.0
R (Å)
Cl-
R
Y
Y=Br-
14. [AuBr4]-···Cl-
(o)
310
280
250
220
ΔEb (kJ/mol)
2.6
3.4
4.2
5.0
R (Å)
Br-
R
Y
Y=Br-
15. [AuBr4]-···Br-
(p)
324
298
272
246
220
ΔEb (kJ/mol)
2.8
3.5
4.2
4.9
R (Å)
I-
R
Y
Y=Br-
16. [AuBr4]-···I-
(q)
258
244
230
216
ΔEb (kJ/mol)
2.4
3.2
4.0
4.8
R (Å)
N
C
R
Y
Y=Br-
17. [AuBr4]-···CN-
(r)
263
247
231
215
ΔEb (kJ/mol)
2.4
3.2
4.0
4.8
R (Å)
O
Cl
R
Y
Y=Br-
18. [AuBr4]-···OCl-


(s)
19. [AuI4]⁻···F⁻
ΔEb (kJ/mol)
R (Å)
(t)
20. [AuI4]⁻···Cl⁻
(u)
21. [AuI4]⁻···Br⁻
(v)
22. [AuI4]⁻···I⁻
(w)
23. [AuI4]⁻···CN⁻
(x)
24. [AuI4]⁻···OCl⁻
Y=I⁻


(y)
F⁻
R
Au
Y=CN⁻
25. [Au(CN)2]⁻···F⁻
ΔEb (kJ/mol)
R (Å)
(z)
Au
R
F⁻
-38.7 kJ/mol
26. [AuO]⁻···F⁻
(aa)
-17.9 kJ/mol
Ag
27. [Ag(CN)2]⁻···F⁻
(ab)
28. [Au(CN)4]⁻··· [Au(CN)4]⁻
(ac)
RI-DLPNO-CCSD//ωB97x-D2/def2-TZVP
RI-DLPNO-CCSD/def2-QZVPP//
SCS-MP2/def2-QZVP
Y=Cl⁻
29. [AuCl4]⁻··· [AuCl4]⁻
(ad)
Y=Br⁻
30. [AuBr4]⁻··· [AuBr4]⁻

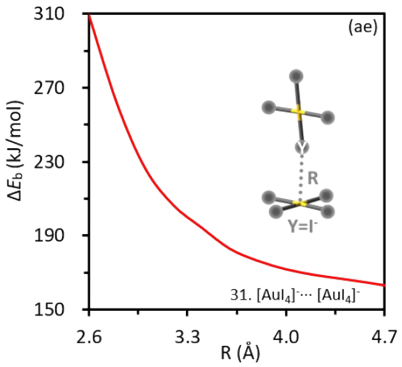


Fig. S2. Profiles of binding energy along with the variation in inter-anion distance calculated at RI-DLPNO-CCSD//ωB97x-D2/def2-TZVP theoretical level. RI-DLPNO-CCSD//def2-QZVPP//SCS-MP2/def2-QZVP theoretical level (s) were also employed for complex $[AuCl_4]^{-}\cdots[AuCl_4]^{-}$ in order to confirm the absence of metastability.

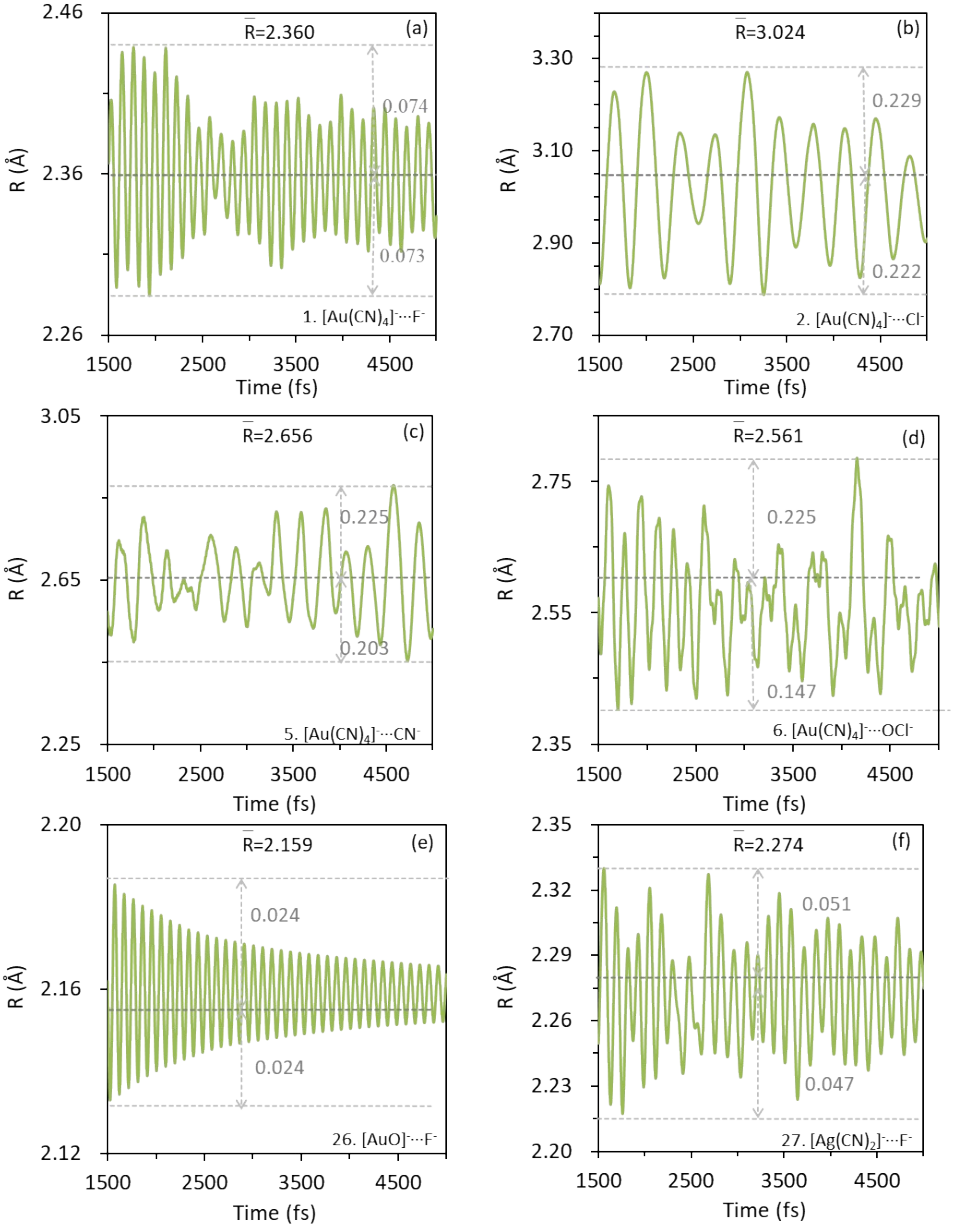


Fig. S3. Evolutions of the inter-anion distance over time (after the 1500st fs) in the AIMD simulation, with the averaged value ($\bar{R}$), and the corresponding maximal and minimum deviations denoted.

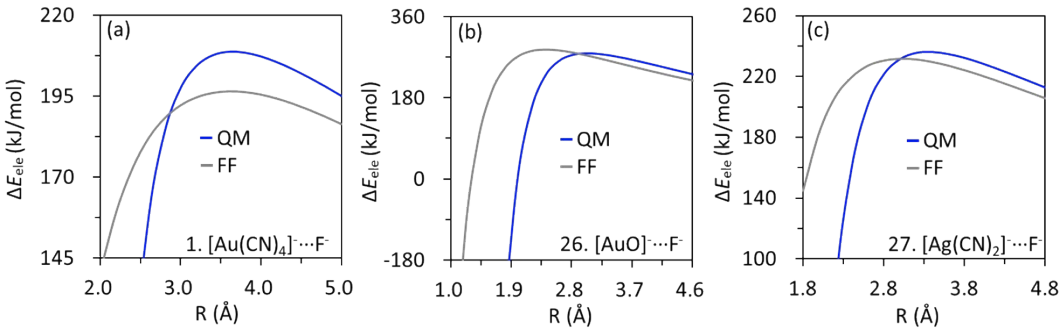


Fig. S4. The electrostatic interaction along the inter-anion distance calculated using the BLW-ED method (in blue) and AMOEBA polarizable force field (in grey).

Additional Tables

Table S1. Polarizabilities (along the direction of CiBs) of optimized and deformed monomers (α, in a.u.) at ωB97x-D2/def2-TZVP(-PP) theoretical level.

No.	Optimized monomer	α	No.	Deformed monomer	α
1	$[Au(CN)_4]^-$	115.564	**1**	$[Au(CN)_4]^-\cdots F^-$	116.553
2	-	-	**2**	$[Au(CN)_4]^-\cdots Cl^-$	116.070
5	-	-	**5**	$[Au(CN)_4]^-\cdots CN^-$	116.500
6	-	-	**6**	$[Au(CN)_4]^-\cdots OCl^-$	116.238
25	$[Au(CN)_2]^-$	101.970	**25**	$[Au(CN)_2]^-\cdots F^-$	101.512
26	$[AuO]^-$	71.843	**26**	$[AuO]^-\cdots F^-$	73.734
27	$[Ag(CN)_2]^-$	91.148	**27**	$[Ag(CN)_2]^-\cdots F^-$	85.049

Table S2. Amount of charge (ΔQ) transferred from the Lewis base to the acid, calculated using the NPA.

No.	Complexes	ΔQ	No.	Complexes	ΔQ
1	$[Au(CN)_4]^-\cdots F^-$	0.146	**6**	$[Au(CN)_4]^-\cdots OCl^-$	0.122
2	$[Au(CN)_4]^-\cdots Cl^-$	0.143	**26**	$[AuO]^-\cdots F^-$	0.176
5	$[Au(CN)_4]^-\cdots CN^-$	0.258	**27**	$[Ag(CN)_2]^-\cdots F^-$	0.138

Table S3. The distances (Å) of CiBs in the local minimum (R_{LM}) and transition structure (R_{TS}), and well-depthes (in kJ/mol) derived from the binding energy profiles calculated at RI-DLPNO-CCSD//ωB97x-D2/def2-TZVPD theoretical level.

No.	Complexes	R_{LM}	R_{TS}	$\Delta\Delta E_b$
1	$[Au(CN)_4]^-\cdots F^-$	2.400	4.000	-41.3
2	$[Au(CN)_4]^-\cdots Cl^-$	3.000	4.200	-8.2
5	$[Au(CN)_4]^-\cdots CN^-$	2.800	4.000	-15.5
6	$[Au(CN)_4]^-\cdots OCl^-$	2.600	3.800	-18.5
26	$[AuO]^-\cdots F^-$	2.200	3.200	-42.2
27	$[Ag(CN)_2]^-\cdots F^-$	2.400	3.400	-13.7

The xyz coordinates (in Å) of inter-anion CiBs optimized at ωB97x-D2/def2-TZVP level of theory.

1. $[Au(CN)_4]^-\cdots F^-$

Au	79.0	-0.000461	0.000518	0.206966
C	6.0	0.000034	2.014214	0.047677
C	6.0	2.013240	-0.000035	0.048304
C	6.0	0.000031	-2.013183	0.048338
C	6.0	-2.014157	-0.000038	0.047716
N	7.0	0.000909	3.158170	-0.099547
N	7.0	-3.158109	-0.001022	-0.099543
N	7.0	0.000900	-3.157063	-0.099557
N	7.0	3.157125	-0.001013	-0.099552
F	9.0	-0.007496	0.008431	2.566647

2. $[Au(CN)_4]^-\cdots Cl^-$

Au	79.0	-0.001224	0.000091	0.179272
C	6.0	-0.001554	-2.011554	0.030113
C	6.0	2.010583	0.000116	0.032782
C	6.0	-0.001554	2.011710	0.029687
C	6.0	-2.012679	0.000116	0.027058
N	7.0	-0.002046	-3.151602	-0.139194
N	7.0	-3.152482	0.000152	-0.144088
N	7.0	-0.002046	3.151724	-0.139878

N	7.0	3.150845	0.000153	-0.134902
Cl	17.0	-0.000222	0.000016	3.159124

5. $[Au(CN)_4]^-\cdots CN^-$

Au	79.0	-0.004488	0.003146	0.191600
C	6.0	-0.003407	2.015299	-0.001183
C	6.0	2.009075	0.002465	0.012521
C	6.0	-0.003501	-2.010101	0.009480
C	6.0	-2.016301	0.002412	-0.004134
N	7.0	-0.002518	3.155430	-0.171118
N	7.0	-3.156148	0.001845	-0.175868
N	7.0	-0.002689	-3.151148	-0.154288
N	7.0	3.150382	0.001950	-0.149264
N	7.0	-0.020218	0.005275	3.975149
C	6.0	-0.015112	0.009541	2.812064

6. $[Au(CN)_4]^-\cdots OCl^-$

Au	79.0	0.000867	-0.032056	0.222258
C	6.0	-0.010526	1.982920	0.121511
C	6.0	2.011658	-0.018133	0.054943
C	6.0	0.012383	-2.041277	0.039276
C	6.0	-2.013093	-0.036587	0.102172
N	7.0	-0.014785	3.128968	-0.002469
N	7.0	-3.156243	-0.031735	-0.044925
N	7.0	0.023911	-3.179679	-0.141189
N	7.0	3.152810	-0.005628	-0.107394
O	8.0	0.157767	0.039570	2.751409
Cl	17.0	-0.821687	-0.938053	3.683199

26. $[AuO]^-\cdots F^-$

O	8.0	-6.588535	0.261088	0.375474
Au	79.0	-4.691261	0.366706	0.322788
F	9.0	-2.537374	0.472342	0.281211

27. $[Ag(CN)_2]^-\cdots F^-$

Ag	47.0	0.015377	0.713246	0.003829
C	6.0	0.001692	-0.074299	2.027078
N	7.0	-0.012517	-0.539432	3.093811
C	6.0	0.002080	-0.064250	-2.021569
N	7.0	-0.012545	-0.529284	-3.088288
F	9.0	0.041293	2.996897	0.017302