Electronic supplementary information

Facile substitution of bridging SO_2^{2-} ligands in Re_{12} bioctahedral cluster complexes

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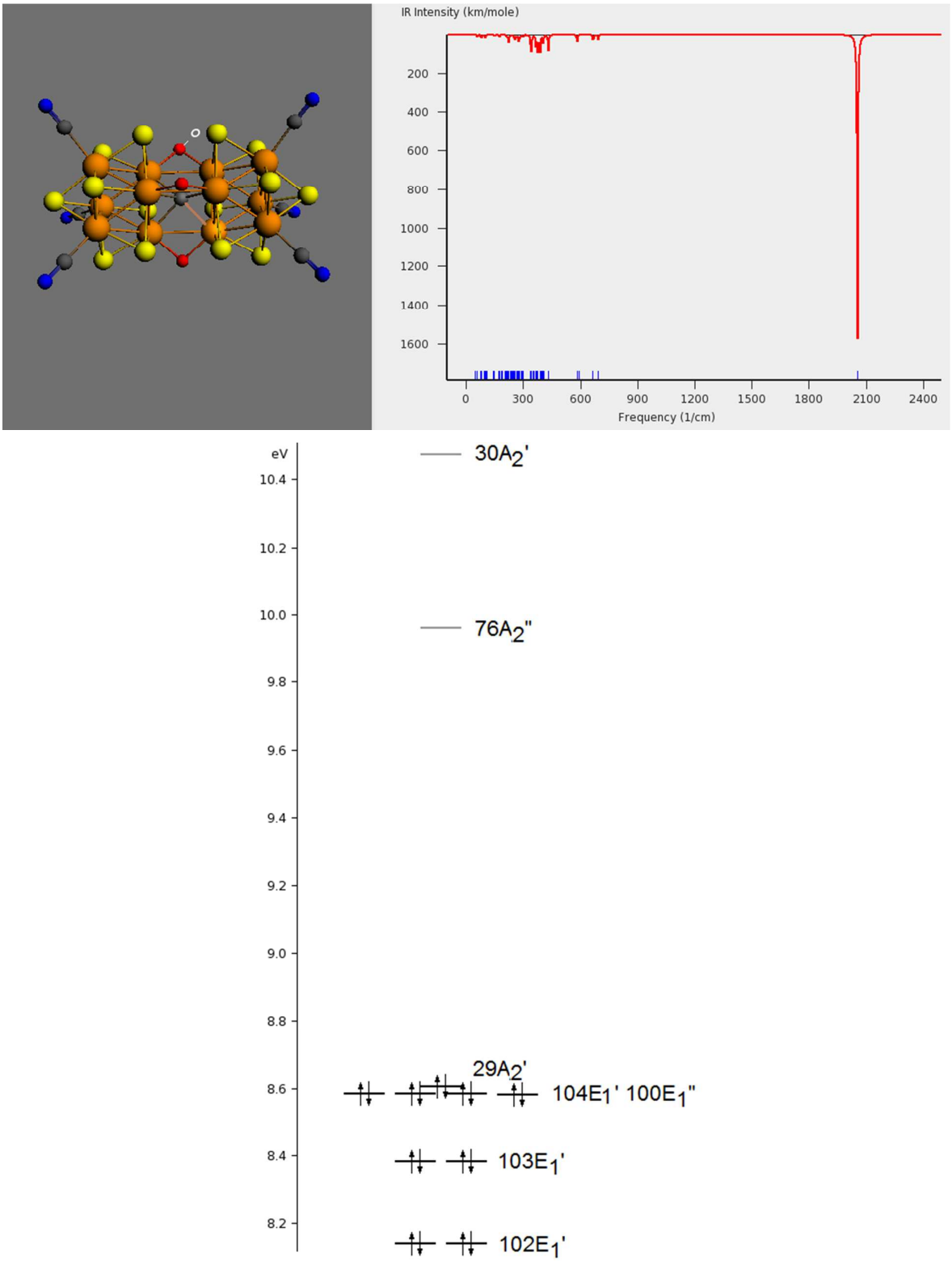
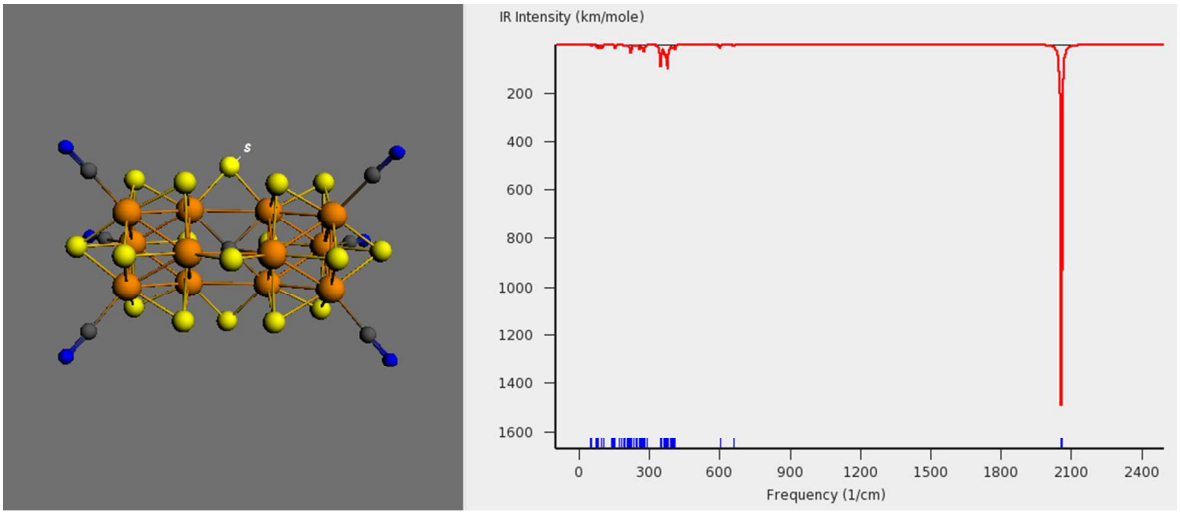


Fig. S1 Optimized coordinates, energy levels of frontier molecular orbitals and calculated infrared spectrum for $[Re_{12}CS_{14}(\mu\text{-}O)_3(CN)_6]^{6-}$ cluster anion

Table S1 List of optimized atomic coordinates (Å) for $[Re_{12}CS_{14}(\mu\text{-}O)_3(CN)_6]^{6-}$ cluster anion

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
1.C	-3.280639	0.000000	-4.845506	22.Re	1.572360	0.000000	-1.419982
2.C	0.000000	0.000000	0.000000	23.Re	-1.533044	0.000000	3.611474
3.C	1.640320	2.841117	-4.845506	24.Re	0.766522	-1.327655	3.611474
4.C	1.640320	-2.841117	-4.845506	25.Re	0.766522	1.327655	3.611474
5.C	-3.280639	0.000000	4.845506	26.S	0.000000	0.000000	-5.527144
6.C	1.640320	-2.841117	4.845506	27.S	-1.416978	-2.454278	3.528194
7.C	1.640320	2.841117	4.845506	28.S	2.833956	0.000000	3.528194
8.N	-4.224197	0.000000	-5.556667	29.S	1.422580	2.463980	1.560468
9.N	2.112099	3.658262	-5.556667	30.S	1.422580	-2.463980	1.560468
10.N	2.112099	-3.658262	-5.556667	31.S	-2.845159	0.000000	1.560468
11.N	-4.224197	0.000000	5.556667	32.O	-1.491993	-2.584208	0.000000
12.N	2.112099	-3.658262	5.556667	33.O	-1.491993	2.584208	0.000000
13.N	2.112099	3.658262	5.556667	34.O	2.983987	0.000000	0.000000
14.Re	-1.533044	0.000000	-3.611474	35.S	-1.416978	2.454278	-3.528194
15.Re	-0.786180	-1.361704	1.419982	36.S	-1.416978	-2.454278	-3.528194
16.Re	-0.786180	1.361704	1.419982	37.S	2.833956	0.000000	-3.528194
17.Re	1.572360	0.000000	1.419982	38.S	1.422580	-2.463980	-1.560468
18.Re	0.766522	1.327655	-3.611474	39.S	-2.845159	0.000000	-1.560468
19.Re	0.766522	-1.327655	-3.611474	40.S	1.422580	2.463980	-1.560468
20.Re	-0.786180	-1.361704	-1.419982	41.S	0.000000	0.000000	5.527144
21.Re	-0.786180	1.361704	-1.419982	42.S	-1.416978	2.454278	3.528194



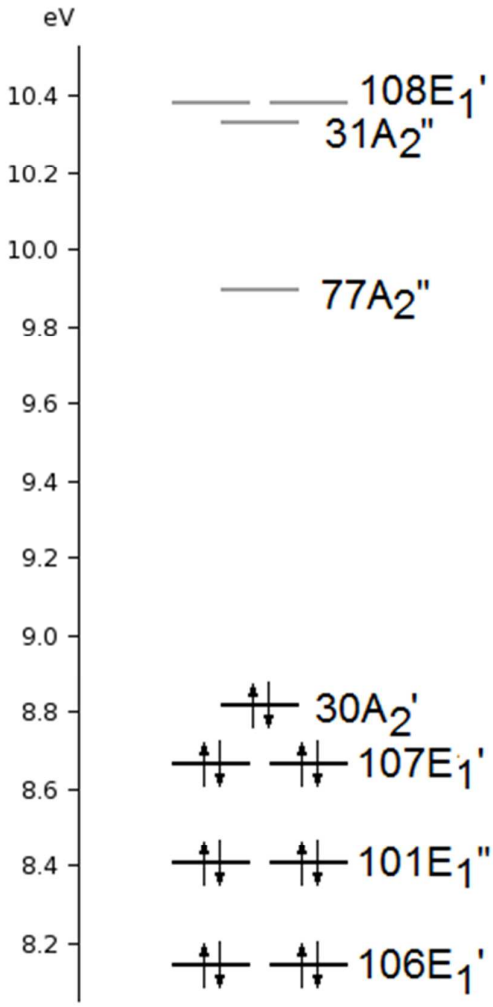


Fig. S2 Optimized coordinates, energy levels of frontier molecular orbitals and calculated infrared spectrum for $[Re_{12}CS_{14}(\mu\text{-}S)_3(CN)_6]^{6-}$ cluster anion

Table S2 List of optimized atomic coordinates (Å) for $[Re_{12}CS_{14}(\mu\text{-}S)_3(CN)_6]^{6-}$ cluster anion

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
1.C	-3.255726	0.000000	-4.918784	22.Re	1.576495	0.000000	-1.480552
2.C	0.000000	0.000000	0.000000	23.Re	-1.533460	0.000000	3.663932
3.C	1.627863	2.819542	-4.918784	24.Re	0.766730	-1.328015	3.663932
4.C	1.627863	-2.819542	-4.918784	25.Re	0.766730	1.328015	3.663932
5.C	-3.255726	0.000000	4.918784	26.S	0.000000	0.000000	-5.580984
6.C	1.627863	-2.819542	4.918784	27.S	-1.410122	-2.442402	3.583509
7.C	1.627863	2.819542	4.918784	28.S	2.820243	0.000000	3.583509
8.N	-4.186709	0.000000	-5.645499	29.S	1.417710	2.455546	1.609617
9.N	2.093354	3.625796	-5.645499	30.S	1.417710	-2.455546	1.609617
10.N	2.093354	-3.625796	-5.645499	31.S	-2.835421	0.000000	1.609617
11.N	-4.186709	0.000000	5.645499	32.O	-1.725536	-2.988717	0.000000
12.N	2.093354	-3.625796	5.645499	33.O	-1.725536	2.988717	0.000000
13.N	2.093354	3.625796	5.645499	34.O	3.451073	0.000000	0.000000
14.Re	-1.533460	0.000000	-3.663932	35.S	-1.410122	2.442402	-3.583509
15.Re	-0.788247	-1.365285	1.480552	36.S	-1.410122	-2.442402	-3.583509
16.Re	-0.788247	1.365285	1.480552	37.S	2.820243	0.000000	-3.583509
17.Re	1.576495	0.000000	1.480552	38.S	1.417710	-2.455546	-1.609617
18.Re	0.766730	1.328015	-3.663932	39.S	-2.835421	0.000000	-1.609617
19.Re	0.766730	-1.328015	-3.663932	40.S	1.417710	2.455546	-1.609617
20.Re	-0.788247	-1.365285	-1.480552	41.S	0.000000	0.000000	5.580984
21.Re	-0.788247	1.365285	-1.480552	42.S	-1.410122	2.442402	3.583509

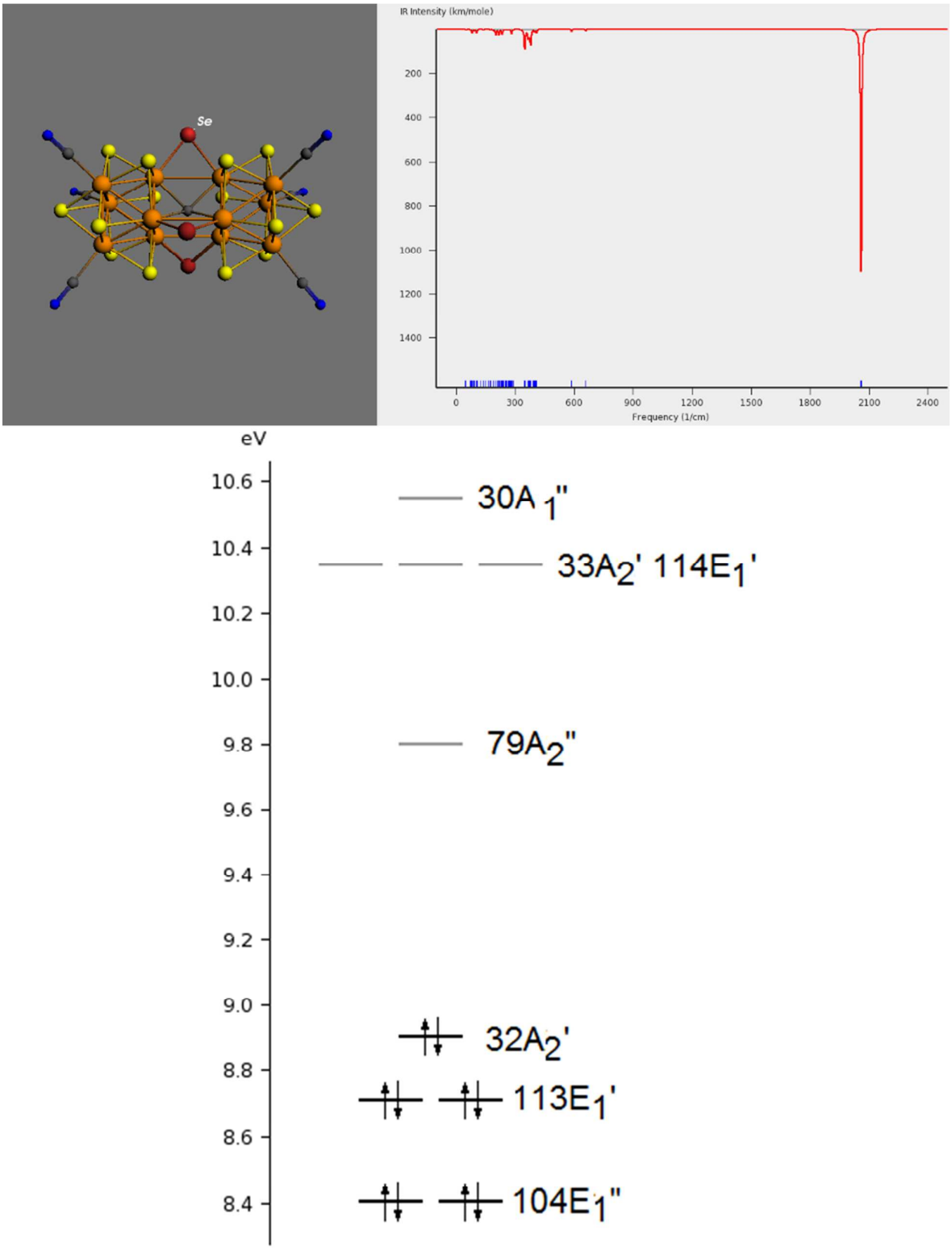


Fig. S3 Optimized coordinates, energy levels of frontier molecular orbitals and calculated infrared spectrum for $[Re_{12}CS_{14}(\mu\text{-}Se)_3(CN)_6]^{6-}$ cluster anion

Table S3 List of optimized atomic coordinates (Å) for $[Re_{12}CS_{14}(\mu\text{-}Se)_3(CN)_6]^{6-}$ cluster anion

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
1.C	-3.250531	0.000000	-4.938741	22.Re	1.571373	0.000000	-1.498234
2.C	0.000000	0.000000	0.000000	23.Re	-1.533306	0.000000	3.678443
3.C	1.625266	2.815043	-4.938741	24.Re	0.766653	-1.327882	3.678443
4.C	1.625266	-2.815043	-4.938741	25.Re	0.766653	1.327882	3.678443
5.C	-3.250531	0.000000	4.938741	26.S	0.000000	0.000000	-5.595139
6.C	1.625266	-2.815043	4.938741	27.S	-1.408989	-2.440441	3.597956
7.C	1.625266	2.815043	4.938741	28.S	2.817979	0.000000	3.597956
8.N	-4.178525	0.000000	-5.669042	29.S	1.415627	2.451939	1.622813
9.N	2.089263	3.618709	-5.669042	30.S	1.415627	-2.451939	1.622813
10.N	2.089263	-3.618709	-5.669042	31.S	-2.831255	0.000000	1.622813
11.N	-4.178525	0.000000	5.669042	32.Se	-1.802393	-3.121837	0.000000
12.N	2.089263	-3.618709	5.669042	33.Se	-1.802393	3.121837	0.000000
13.N	2.089263	3.618709	5.669042	34.Se	3.604786	0.000000	0.000000
14.Re	-1.533306	0.000000	-3.678443	35.S	-1.408989	2.440441	-3.597956
15.Re	-0.785687	-1.360849	1.498234	36.S	-1.408989	-2.440441	-3.597956
16.Re	-0.785687	1.360849	1.498234	37.S	2.817979	0.000000	-3.597956
17.Re	1.571373	0.000000	1.498234	38.S	1.415627	-2.451939	-1.622813
18.Re	0.766653	1.327882	-3.678443	39.S	-2.831255	0.000000	-1.622813
19.Re	0.766653	-1.327882	-3.678443	40.S	1.415627	2.451939	-1.622813
20.Re	-0.785687	-1.360849	-1.498234	41.S	0.000000	0.000000	5.595139
21.Re	-0.785687	1.360849	-1.498234	42.S	-1.408989	2.440441	3.597956

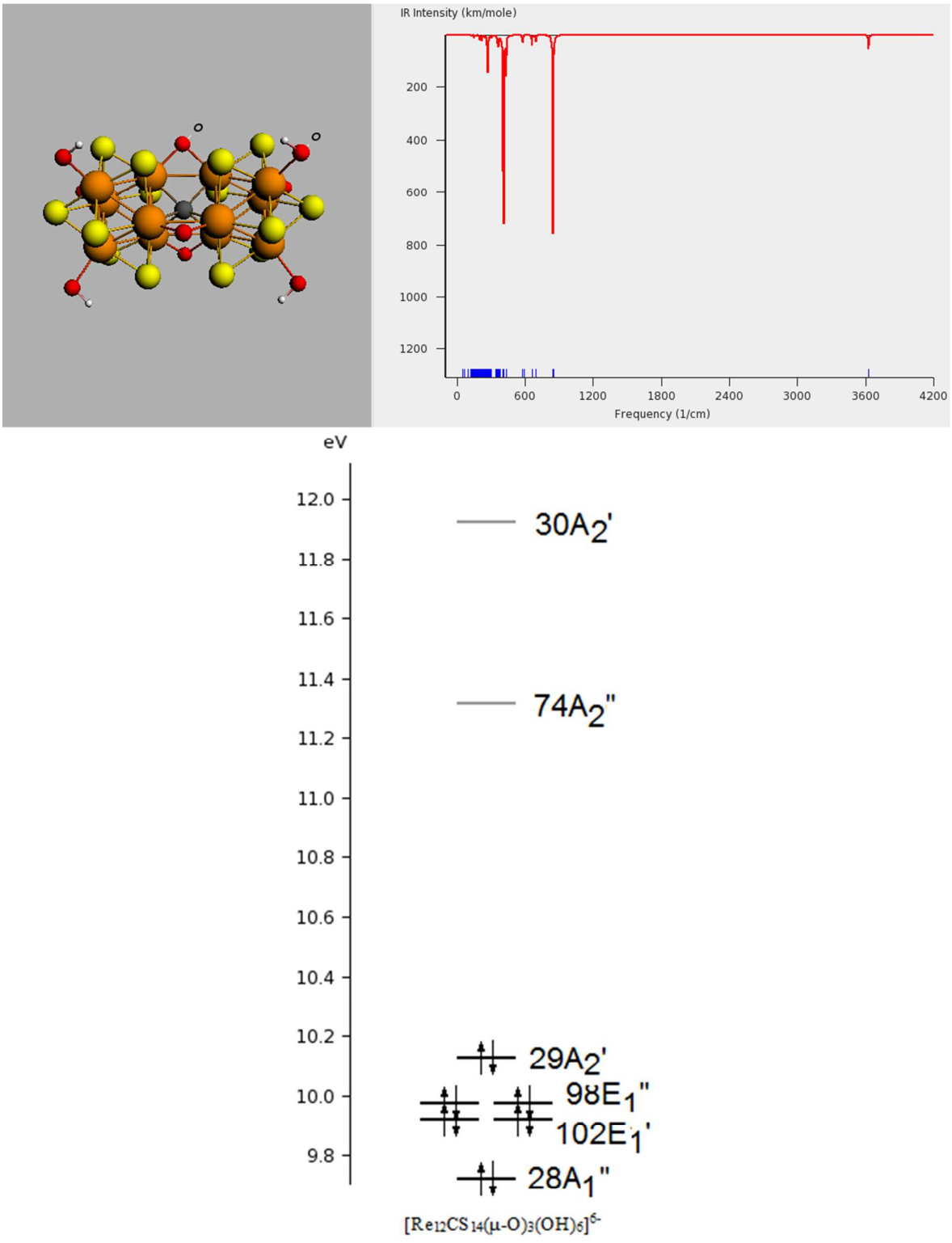


Fig. S4 Optimized coordinates, energy levels of frontier molecular orbitals and calculated infrared spectrum for $[Re_{12}CS_{14}(\mu\text{-}O)_3(OH)_6]^{6-}$ cluster anion

Table S4 List of optimized atomic coordinates (Å) for $[Re_{12}CS_{14}(\mu\text{-}O)_3(OH)_6]^{6-}$ cluster anion

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
1.O	-3.280602	0.000000	-4.796593	22.Re	-0.786549	-1.362343	-1.422571
2.O	1.640301	2.841085	-4.796593	23.Re	-0.786549	1.362343	-1.422571
3.O	-1.497230	-2.593279	0.000000	24.Re	1.573098	0.000000	-1.422571
4.O	-1.497230	2.593279	0.000000	25.Re	-1.522563	0.000000	3.605192
5.O	2.994460	0.000000	0.000000	26.Re	0.761281	-1.318578	3.605192
6.O	1.640301	-2.841085	-4.796593	27.Re	0.761281	1.318578	3.605192
7.O	-3.280602	0.000000	4.796593	28.S	0.000000	0.000000	-5.554438
8.O	1.640301	-2.841085	4.796593	29.S	-1.428795	-2.474746	3.524281
9.O	1.640301	2.841085	4.796593	30.S	2.857590	0.000000	3.524281
10.H	-3.941194	0.000000	-4.076936	31.S	1.427752	2.472938	1.573256
11.H	1.970597	3.413174	-4.076936	32.S	1.427752	-2.472938	1.573256
12.H	1.970597	-3.413174	-4.076936	33.S	-2.855503	0.000000	1.573256
13.H	-3.941194	0.000000	4.076936	34.S	-1.428795	2.474746	-3.524281
14.H	1.970597	-3.413174	4.076936	35.S	-1.428795	-2.474746	-3.524281
15.H	1.970597	3.413174	4.076936	36.S	2.857590	0.000000	-3.524281
16.Re	-1.522563	0.000000	-3.605192	37.S	1.427752	-2.472938	-1.573256
17.Re	-0.786549	-1.362343	1.422571	38.S	-2.855503	0.000000	-1.573256
18.Re	-0.786549	1.362343	1.422571	39.S	1.427752	2.472938	-1.573256
19.Re	1.573098	0.000000	1.422571	40.S	0.000000	0.000000	5.554438
20.Re	0.761281	1.318578	-3.605192	41.S	-1.428795	2.474746	3.524281
21.Re	0.761281	-1.318578	-3.605192	42.C	0.000000	0.000000	0.000000

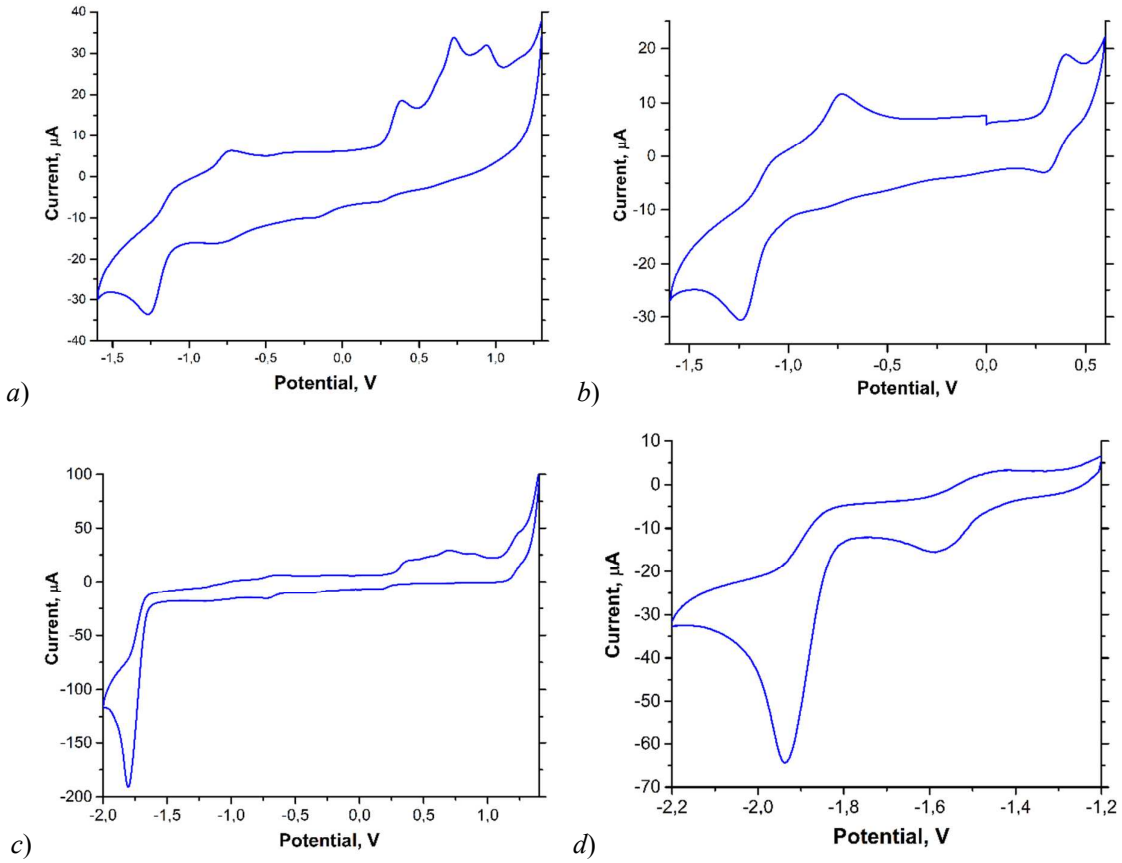


Fig. S5 The wide range cyclic voltammograms showing the reduction and oxidation of $[Re_{12}CS_{14}(\mu\text{-}S)_3(CN)_6]^{n-}$ (*a*, *b*) and $[Re_{12}CSe_{14}(\mu\text{-}Se)_3(CN)_6]^{n-}$ (*c, d*) anions in acetonitrile *vs* Ag/AgCl electrode at the scan rates of 200 $mV \cdot s^{-1}$ for *a*)–*c*) and 150 $mV \cdot s^{-1}$ for *d*).