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Synthesis, structures, redox properties, and theoretical calculations of thiohalide capped octahedral Hexanuclear technetium(III) clusters

Takashi Yoshimura,[*,a,b] *Kojiro Nagata,*[a] *Ayumi Matsuda,*[c] *Toshiki Omote,*[c] *Yasushi Kino,*[d] *Tsutomu Takayama,*[e] *Tsutomu Sekine,*[f] *Atsushi Shinohara*[b,c]

[a.] *Radioisotope Research Center, Institute for Radiation Sciences, Osaka University, Suita 565-0871, Japan,* [b.] *Project Research Center for Fundamental Sciences, Graduate School of Science, Osaka University, Toyonaka, Osaka 560-0043, Japan,* [c.] *Department of Chemistry, Graduate School of Science, Osaka University, Toyonaka 560-0043, Japan,* [d.] *Department of Chemistry, Graduate School of Science, Tohoku University, Sendai, Miyagi 980-8576, Japan,* [e.] *Department of Chemistry, Daido University, Nagoya, Aichi 457-8530, Japan,* [f.] *Institute for Excellence in Higher Education, Tohoku University, Sendai, Miyagi 980-8576, Japan.*

Table S1. Calculated Energies and Components of MOs Near Frontier Orbital Levels of D_{3d} isomers for $[M_6(\mu_3\text{-}S)_6(\mu_3\text{-}Br)_2Br_6]^{2-}$ (M = Tc, Re)

	$[Tc_6(\mu_3\text{-}S)_6(\mu_3\text{-}Br)_2Br_6]^{2-}$ (D_{3d} isomer)					$[Re_6(\mu_3\text{-}S)_6(\mu_3\text{-}Br)_2Br_6]^{2-}$ (D_{3d} isomer)				
	Energy/eV	Tc	S	Br_{cap}	$Br_{terminal}$	Energy/eV	Re	S	Br_{cap}	$Br_{terminal}$
LUMO+6	-3.04	0.80	0.20			-2.19	0.58	0.21	0.21	
LUMO+5	-3.25	0.85	0.15			-2.38	0.87	0.13		
LUMO+4	-3.39	0.78	0.11	0.11		-2.65	0.89		0.06	0.05
LUMO+3	-3.39	0.79	0.11	0.10		-2.65	0.90		0.06	0.04
LUMO+2	-3.46	0.90		0.05	0.05	-2.66	0.78	0.10	0.12	
LUMO+1	-3.46	0.91		0.06	0.03	-2.66	0.78	0.09	0.12	0.01
LUMO	-3.85	1.00				-2.81	1.00			
HOMO	-6.53	0.22	0.27		0.51	-6.27	0.68	0.32		
HOMO-1	-6.53	0.23	0.28		0.49	-6.27	0.66	0.34		
HOMO-2	-6.59	0.54	0.28		0.19	-6.41	0.26	0.27		0.47
HOMO-3	-6.59	0.54	0.28		0.19	-6.41	0.28	0.27		0.45
HOMO-4	-6.61		0.53		0.47	-6.49	0.28	0.13		0.59
HOMO-5	-6.65	0.17	0.12		0.71	-6.59		0.56		0.44
HOMO-6	-6.87	0.17	0.07	0.08	0.68	-6.74	0.25	0.11	0.09	0.55

Table S2. Calculated Energies and Components of MOs Near Frontier Orbital Levels of *syn*-C_{2v} isomers for $[M_6(\mu_3\text{-}S)_6(\mu_3\text{-}Br)_2Br_6]^{2-}$ (M = Tc, Re)

	$[Tc_6(\mu_3\text{-}S)_6(\mu_3\text{-}Br)_2Br_6]^{2-}$ (*syn*-C_{2v} isomer)					$[Re_6(\mu_3\text{-}S)_6(\mu_3\text{-}Br)_2Br_6]^{2-}$ (*syn*-C_{2v} isomer)				
	Energy/eV	Tc	S	Br_{cap}	$Br_{terminal}$	Energy/eV	Re	S	Br_{cap}	$Br_{terminal}$
LUMO+6	-2.93	0.78	0.22			-2.08	0.80	0.20		
LUMO+5	-3.00	0.81	0.19			-2.15	0.61	0.15	0.14	0.10
LUMO+4	-3.25	0.89	0.05	0.06		-2.45	0.88	0.04	0.08	
LUMO+3	-3.40	0.86	0.06	0.05	0.03	-2.55	0.91		0.06	0.03
LUMO+2	-3.45	0.96		0.04		-2.63	0.95		0.05	
LUMO+1	-3.55	0.88		0.09	0.03	-2.72	1.00			
LUMO	-3.79	1.00				-2.72	0.85		0.12	0.03
HOMO	-6.45	0.45	0.35		0.20	-6.11	0.64	0.36		
HOMO-1	-6.52	0.17	0.30		0.53	-6.20	0.71	0.27	0.02	
HOMO-2	-6.53	0.15	0.36		0.49	-6.35	0.29	0.26		0.45
HOMO-3	-6.59	0.31	0.16		0.53	-6.37	0.30	0.20		0.50
HOMO-4	-6.60	0.14	0.42		0.44	-6.44	0.32	0.17	0.03	0.48
HOMO-5	-6.62	0.55	0.33		0.12	-6.45	0.19	0.45		0.36
HOMO-6	-6.63	0.40	0.19		0.41	-6.50	0.17	0.43		0.40

Table S3. Calculated Energies and Components of MOs Near Frontier Orbital Levels of *fac*-C_{2v} isomers for $[M_6(\mu_3\text{-}S)_6(\mu_3\text{-}Br)_2Br_6]^{2-}$ (M = Tc, Re)

	$[Tc_6(\mu_3\text{-}S)_6(\mu_3\text{-}Br)_2Br_6]^{2-}$ (*fac*-C_{2v} isomer)					$[Re_6(\mu_3\text{-}S)_6(\mu_3\text{-}Br)_2Br_6]^{2-}$ (*fac*-C_{2v} isomer)				
	Energy/eV	Tc	S	Br_{cap}	$Br_{terminal}$	Energy/eV	Re	S	Br_{cap}	$Br_{terminal}$
LUMO+6	-3.00	0.77	0.23			-2.09	0.82	0.18		
LUMO+5	-3.02	0.79	0.21			-2.14	0.72	0.19		0.09
LUMO+4	-3.20	0.67		0.22	0.11	-2.47	0.87	0.08	0.05	
LUMO+3	-3.32	0.92	0.08			-2.64	0.66		0.27	0.07
LUMO+2	-3.54	0.86		0.09	0.05	-2.69	1.00			
LUMO+1	-3.60	0.90		0.10		-2.77	0.90		0.10	
LUMO	-3.77	1.00				-2.82	0.87		0.13	
HOMO	-6.50	0.22	0.25		0.53	-6.18	0.73	0.27		
HOMO-1	-6.52	0.12	0.49		0.39	-6.22	0.69	0.31		
HOMO-2	-6.53	0.21	0.31		0.48	-6.32	0.30	0.25		0.45
HOMO-3	-6.54	0.54	0.32		0.14	-6.38	0.28	0.24		0.48
HOMO-4	-6.57	0.16	0.25		0.59	-6.39	0.28	0.21		0.51
HOMO-5	-6.61	0.55	0.18		0.27	-6.45	0.12	0.48		0.40
HOMO-6	-6.68	0.18	0.35		0.47	-6.46	0.24	0.38		0.38

Table S4. Calculated Energies and Components of MOs Near Frontier Orbital Levels for $[M_6(\mu_3\text{-}S)_7(\mu_3\text{-}Br)Br_6]^{3-}$ (M = Tc, Re)

	$[Tc_6(\mu_3\text{-}S)_7(\mu_3\text{-}Br)Br_6]^{3-}$					$[Re_6(\mu_3\text{-}S)_7(\mu_3\text{-}Br)Br_6]^{3-}$				
	Energy/eV	Tc	S	Br_{cap}	$Br_{terminal}$	Energy/eV	Re	S	Br_{cap}	$Br_{terminal}$
LUMO+6	-2.50	0.60	0.15	0.07	0.18	-1.65	0.75	0.19		0.06
LUMO+5	-2.54	0.80	0.20			-1.65	0.77	0.17		0.06
LUMO+4	-2.54	0.80	0.20			-1.84	0.60	0.16	0.10	0.14
LUMO+3	-2.76	0.82	0.18			-1.84	0.86	0.14		
LUMO+2	-3.01	0.91	0.03	0.06		-2.19	1.00			
LUMO+1	-3.01	0.89	0.04	0.07		-2.21	0.90	0.01	0.08	
LUMO	-3.28	1.00				-2.21	0.90	0.01	0.08	
HOMO	-6.09	0.68	0.32			-5.68	0.70	0.30		
HOMO-1	-6.09	0.70	0.30			-5.68	0.70	0.30		
HOMO-2	-6.25	0.12	0.52		0.36	-6.07	0.38	0.20		0.42
HOMO-3	-6.25	0.14	0.53		0.33	-6.07	0.39	0.19		0.42
HOMO-4	-6.28		0.55		0.45	-6.13	0.38	0.15		0.47
HOMO-5	-6.29	0.33	0.18		0.49	-6.15	0.18	0.51		0.31
HOMO-6	-6.29	0.32	0.18		0.50	-6.15	0.17	0.51		0.32

Table S5. Calculated Energies and Components of MOs Near Frontier Orbital Levels for $[M_6(\mu_3\text{-}S)_7(\mu_3\text{-}Cl)Cl_6]^{3-}$ (M = Tc, Re)

	$[Tc_6(\mu_3\text{-}S)_7(\mu_3\text{-}Cl)Cl_6]^{3-}$					$[Re_6(\mu_3\text{-}S)_7(\mu_3\text{-}Cl)Cl_6]^{3-}$				
	Energy/eV	Tc	S	Cl_{cap}	$Cl_{terminal}$	Energy/eV	Re	S	Cl_{cap}	$Cl_{terminal}$
LUMO+6	-2.53	0.78	0.22			-1.60	0.81	0.19		
LUMO+5	-2.58	0.80	0.20			-1.60	0.85	0.15		
LUMO+4	-2.58	0.80	0.20			-1.69	0.61	0.21	0.08	0.10
LUMO+3	-2.79	0.82	0.18			-1.82	0.84	0.16		
LUMO+2	-3.03	0.91	0.04	0.05		-2.14	0.91	0.02	0.06	0.01
LUMO+1	-3.03	0.92	0.03	0.05		-2.14	0.91	0.01	0.07	0.01
LUMO	-3.33	1.00				-2.21	1.00			
HOMO	-6.15	0.70	0.30			-5.71	0.70	0.30		
HOMO-1	-6.15	0.69	0.31			-5.71	0.69	0.31		
HOMO-2	-6.37	0.21	0.60		0.19	-6.18	0.45	0.23		0.32
HOMO-3	-6.37	0.21	0.59		0.20	-6.18	0.46	0.23		0.31
HOMO-4	-6.41	0.07	0.65		0.28	-6.22	0.22	0.57		0.21
HOMO-5	-6.45	0.38	0.27		0.35	-6.22	0.22	0.57		0.21
HOMO-6	-6.45	0.36	0.28		0.36	-6.22	0.47	0.20		0.33

Table S6. Calculated Energies and Components of MOs Near Frontier Orbital Levels for $[Tc_6(\mu_3\text{-}S)_8Br_6]^{4-}$

	Energy/eV	Tc	S	$Br_{terminal}$
LUMO+6	-2.10	0.71	0.13	0.16
LUMO+5	-2.10	0.71	0.13	0.16
LUMO+4	-2.10	0.69	0.16	0.15
LUMO+3	-2.36	0.82	0.18	
LUMO+2	-2.36	0.86	0.14	
LUMO+1	-2.36	0.90	0.10	
LUMO	-2.81	1.00		
HOMO	-5.68	0.76	0.24	
HOMO-1	-5.68	0.82	0.18	
HOMO-2	-5.99	0.20	0.57	0.23
HOMO-3	-5.99	0.20	0.56	0.24
HOMO-4	-5.99	0.20	0.67	0.23
HOMO-5	-6.06	0.05	0.53	0.42
HOMO-6	-6.06		0.59	0.41
HOMO-7	-6.06		0.59	0.41

Table S7. Atomic Coordinates of Optimized Geometry for $[Tc_6(\mu_3\text{-}S)_6(\mu_3\text{-}Br)_2Br_6]^{2-}$ (D_{3d} isomer)

	x/Å	y/Å	z/Å
S1	0.05157803	0.02976024	-0.02954342
S2	4.89882197	0.02976024	-0.02954342
S3	2.47520000	4.22759663	-0.02951994
S4	2.47520000	-1.36950781	-1.95049366
S5	0.05157803	2.82832857	-1.95047018
S6	4.89882197	2.82832857	-1.95047018
Tc1	3.81477467	2.20244230	0.06610030
Tc2	2.47520000	2.97585791	-2.04610092
Tc3	1.13562533	0.65564652	-2.04611390
Tc4	3.81477467	0.65564652	-2.04611390
Tc5	2.47520000	-0.11776910	0.06608733
Tc6	1.13562533	2.20244230	0.06610030
Br1	2.47520000	1.42906270	-4.25982164
Br2	2.47520000	1.42902612	2.27980805
Br3	-0.71653099	-0.41368829	-3.50206736
Br4	2.47520000	-2.25646314	1.52202284
Br5	5.66693099	-0.41368829	-3.50206736
Br6	5.66693099	3.27177711	1.52205376
Br7	2.47520000	5.11455195	-3.50203644
Br8	-0.71653099	3.27177711	1.52205376

Table S8. Atomic Coordinates of Optimized Geometry for $[Tc_6(\mu_3\text{-}S)_6(\mu_3\text{-}Br)_2Br_6]^{2-}$ (*syn*-C_{2v} isomer)

	x/Å	y/Å	z/Å
S1	0.02685485	0.04171446	-0.04193331
S2	3.47095550	0.04170977	-0.04192860
S3	0.05249246	3.46669267	-0.04863551
S4	0.05249246	0.02803622	-3.46689076
S5	3.44532723	3.46668805	-0.04863087
S6	3.44532723	0.02803161	-3.46688612
Tc1	-0.12026042	1.71507259	-1.72527855
Tc2	1.74891233	1.68623240	-3.62974793
Tc3	3.61807994	1.71506750	-1.72527343
Tc4	1.74891233	3.61967986	-1.70777142
Tc5	1.74890727	1.74173909	0.11971618
Tc6	1.74890727	-0.13004816	-1.74096595
Br1	-2.70366944	1.65556436	-1.66541516
Br2	1.74891572	1.58654159	-6.20912701
Br3	3.63798664	3.62152969	-3.64311397
Br4	-0.14015669	3.62153483	-3.64311915
Br5	1.74890370	1.72585732	2.71234017
Br6	1.74891572	6.19960648	-1.62343096
Br7	6.20148863	1.65555224	-1.66540297
Br8	1.74890370	-2.72253175	-1.70965706

Table S9. Atomic Coordinates of Optimized Geometry for $[Tc_6(\mu_3\text{-}S)_6(\mu_3\text{-}Br)_2Br_6]^{2-}$ (*fac*-C_{2v} isomer)

	x/Å	y/Å	z/Å
S1	0.03381775	0.03377180	-0.04067352
S2	3.45513683	0.03995973	-0.05005997
S3	0.04519526	3.45507757	-0.05005403
S4	3.46575060	3.46050278	0.02290054
S5	3.49878978	0.05910935	-3.43877789
S6	0.06440518	3.49870733	-3.43877191
Tc1	-0.10603878	1.78187066	-1.72689706
Tc2	1.78303872	1.78034766	-3.59415913
Tc3	3.63715854	1.74391343	-1.69252932
Tc4	1.74942024	3.63451731	-1.69252603
Tc5	1.74841031	1.74576525	0.13923426
Tc6	1.78169953	-0.10873322	-1.72690035
Br1	1.80712666	1.80440361	-6.19115323
Br2	1.71533109	6.21576623	-1.59555800
Br3	1.81442777	-2.69134124	-1.67714536
Br4	1.72438173	1.72176858	2.72982903
Br5	6.21835296	1.70590880	-1.59556585
Br6	-2.68859410	1.81851619	-1.67713752
Br7	-0.07353093	-0.07340781	-3.70066371
Br8	3.64094587	3.63543886	-3.63185573

Table S10. Atomic Coordinates of Optimized Geometry for $[Tc_6(\mu_3\text{-}S)_7(\mu_3\text{-}Br)Br_6]^{3-}$

	x/Å	y/Å	z/Å
S1	0.03332956	0.03316141	-0.03300186
S2	3.47584492	0.04339807	-0.04320684
S3	0.05967778	3.47559126	-0.04317072
S4	0.05966182	0.05940693	-3.47534681
S5	3.47524129	3.45900152	-0.01496432
S6	3.47522528	0.03110748	-3.45890493
S7	0.04734848	3.47506525	-3.45886870
Tc1	-0.10886705	1.75479664	-1.74661472
Tc2	1.74311288	1.73499887	-3.61572005
Tc3	3.63189385	1.72614770	-1.71811665
Tc4	1.74312170	3.62378052	-1.71809668
Tc5	1.75427110	1.74606564	0.12522609
Tc6	1.75426240	-0.11707318	-1.74663441
Br1	1.70692701	6.26336379	-1.66975821
Br2	3.66514332	3.64805489	-3.63106913
Br3	6.27127932	1.67759903	-1.66980646
Br4	1.70690569	1.69898852	-6.25550012
Br5	-2.75401331	1.75213728	-1.74395545
Br6	1.73922320	-2.76217806	-1.74400294
Br7	1.73924418	1.73108105	2.77028990

Table S11. Atomic Coordinates of Optimized Geometry for $[Tc_6(\mu_3\text{-}S)_7(\mu_3\text{-}Cl)Cl_6]^{3-}$

	x/Å	y/Å	z/Å
S1	0.03231352	0.03208997	-0.03185898
S2	3.48433182	0.04191588	-0.04164048
S3	0.06739800	3.48394404	-0.04161137
S4	0.06737135	0.06692139	-3.48355136
S5	3.48361375	3.45822804	-0.00692789
S6	3.48358702	0.03202553	-3.45811468
S7	0.05747358	3.48330073	-3.45808549
Cl1	1.77283440	1.75997257	-6.07537098
Cl2	1.74109655	-2.59705063	-1.74735578
Cl3	-2.58426779	1.76007966	-1.74731893
Cl4	1.74113029	1.72842615	2.60966289
Cl5	1.77286816	6.08798296	-1.71580021
Cl6	6.10076605	1.72830052	-1.71583708
Cl7	3.58331261	3.55722985	-3.53150670
Tc1	-0.10630547	1.75768894	-1.74496470
Tc2	1.75345072	1.74070935	-3.60991710
Tc3	3.63516147	1.72693889	-1.71446622
Tc4	1.75346539	3.62245435	-1.71445019
Tc5	1.75685205	1.74405425	0.13179747
Tc6	1.75683752	-0.11913718	-1.74498057

Table S12. Atomic Coordinates of Optimized Geometry for $[Tc_6(\mu_3\text{-}S)_8Br_6]^{4-}$

	x/Å	y/Å	z/Å
S1	0.03611597	0.03611597	-0.03614227
S2	3.47182022	0.03611597	-0.03612473
S3	0.03611597	3.47182022	-0.03612473
S4	0.03613350	0.03613350	-3.47184653
S5	3.47182022	3.47182022	-0.03610720
S6	3.47183776	0.03613350	-3.47182899
S7	0.03613350	3.47183776	-3.47182899
S8	3.47183776	3.47183776	-3.47181145
Tc1	-0.11612534	1.75397686	-1.75398641
Tc2	1.75398641	1.76398641	-3.62407906
Tc3	3.62407906	1.75397686	-1.75396731
Tc4	1.75397686	3.62407906	-1.75396731
Tc5	1.75396731	1.75396731	0.11612534
Tc6	1.75397686	-0.11612534	-1.75398641
Br1	1.75397686	6.35508525	-1.75395337
Br2	6.35508525	1.75397686	-1.75395337
Br3	1.75400035	1.75400035	-6.35508525
Br4	-2.84713153	1.75397686	-1.75400035
Br5	1.75397686	-2.84713153	-1.75400035
Br6	1.75395337	1.75395337	2.84713153

Table S13. Atomic Coordinates of Optimized Geometry for $[Re_6(\mu_3\text{-}S)_7(\mu_3\text{-}Br)Br_6]^{3-}$

	x/Å	y/Å	z/Å
S1	0.02297479	0.02285837	-0.02274504
S2	3.48117088	0.02969786	-0.02957188
S3	0.04599928	3.48098465	-0.02952915
S4	0.04598010	0.04579907	-3.48080202
S5	3.47846365	3.46221217	-0.00357640
S6	3.47844442	0.01973981	-3.46217017
S7	0.03598608	3.47834754	-3.46212734
Br1	1.75121419	6.25865649	-1.71386037
Br2	3.67308616	3.65597093	-3.63894301
Br3	6.26677224	1.72191490	-1.71391654
Br4	1.75118897	1.74308006	-6.25058366
Br5	-2.75984311	1.74774875	-1.73957978
Br6	1.73480079	-2.76798059	-1.73963570
Br7	1.73482590	1.72668161	2.77607542
Re1	1.75038461	-0.12869161	-1.74283388
Re2	-0.12051014	1.75097996	-1.74281061
Re3	1.75039506	1.74221077	0.13683010
Re4	1.74254383	1.73444267	-3.61670856
Re5	3.63287385	1.72558243	-1.71755233
Re6	1.74255439	3.62476983	-1.71752882

Table S14. Atomic Coordinates of Optimized Geometry for $[Re_6(\mu_3\text{-}S)_7(\mu_3\text{-}Cl)Cl_6]^{3-}$

	x/Å	y/Å	z/Å
S1	0.02392582	0.02376248	-0.02358263
S2	3.49182939	0.02999834	-0.02979312
S3	0.05553661	3.49152764	-0.02976550
S4	0.05551685	0.05515087	-3.49121142
S5	3.48919280	3.46376549	0.00309066
S6	3.48917301	0.02207418	-3.46370857
S7	0.04756582	3.48895692	-3.46368090
Cl1	1.81595971	1.80277965	-6.06591444
Cl2	1.73895116	-2.59376970	-1.74518925
Cl3	-2.58100094	1.75790861	-1.74515452
Cl4	1.73897600	1.72628799	2.60638425
Cl5	1.81598430	6.07885544	-1.75864370
Cl6	6.09195558	1.77148096	-1.75867808
Cl7	3.58874361	3.56261877	-3.53682948
Re1	1.75519078	-0.12800338	-1.74339349
Re2	1.75550654	1.74274764	-3.61286232
Re3	-0.11518180	1.75610541	-1.74337845
Re4	1.75551736	3.62543212	-1.71644323
Re5	1.75520153	1.74241490	0.14066992
Re6	3.63815583	1.72896735	-1.71645837

Table S15. Atomic Coordinates of Optimized Geometry for $[Re_6(\mu_3\text{-}S)_6(\mu_3\text{-}Br)_2Br_6]^{2-}$ (D_{3d} isomer)

	x/Å	y/Å	z/Å
S1	0.03933248	0.02269102	-0.02404938
S2	4.91106752	0.02269102	-0.02404938
S3	2.47520000	4.24173733	-0.02402252
S4	2.47520000	-1.38364545	-1.95598735
S5	0.03933248	2.83540086	-1.95596048
S6	4.91106752	2.83540086	-1.95596048
Br1	2.47520000	1.42906690	-4.28020371
Br2	2.47520000	1.42902499	2.30019385
Br3	-0.68650259	-0.39634754	-3.55964616
Br4	2.47520000	-2.22179011	1.57960142
Br5	5.63690259	-0.39634754	-3.55964616
Br6	5.63690259	3.25443942	1.57963630
Br7	2.47520000	5.07988199	-3.55961129
Br8	-0.68650259	3.25443942	1.57963630
Re1	2.47520000	2.97715102	-2.05403788
Re2	3.81589246	2.20308832	0.07404280
Re3	3.81589246	0.65500357	-2.05405267
Re4	2.47520000	-0.11905914	0.07402802
Re5	1.13450754	0.65500357	-2.05405267
Re6	1.13450754	2.20308832	0.07404280

Table S16. Atomic Coordinates of Optimized Geometry for $[Re_6(\mu_3\text{-}S)_6(\mu_3\text{-}Br)_2Br_6]^{2-}$ (*syn*-C_{2v} isomer)

	x/Å	y/Å	z/Å
S1	0.01768688	0.02599025	-0.02611212
S2	3.48012057	0.02598677	-0.02610862
S3	0.04318183	3.46856704	-0.03366936
S4	0.04318183	0.01306913	-3.46867296
S5	3.45463256	3.46856361	-0.03366591
S6	3.45463256	0.01306570	-3.46866951
Br1	-2.71040476	1.69222598	-1.70228913
Br2	1.74891162	1.66572676	-6.20326468
Br3	3.65395445	3.62708528	-3.64869242
Br4	-0.15613243	3.62708911	-3.64869627
Br5	1.74890264	1.71842051	2.72716226
Br6	1.74891162	6.19327952	-1.70256451
Br7	6.20821895	1.69221701	-1.70228012
Br8	1.74890264	-2.73730287	-1.70213454
Re1	1.74890904	3.61380318	-1.71091371
Re2	3.62433615	1.71126423	-1.72144098
Re3	1.74890528	-0.14570845	-1.73310448
Re4	-0.12652189	1.71126801	-1.72144477
Re5	1.74890904	1.68941987	-3.62388365
Re6	1.74890528	1.73397376	0.13542947

Table S17. Atomic Coordinates of Optimized Geometry for $[Re_6(\mu_3\text{-}S)_6(\mu_3\text{-}Br)_2Br_6]^{2-}$ (*fac*-C_{2v} isomer)

	x/Å	y/Å	z/Å
S1	0.02486063	0.02482604	-0.02234194
S2	3.46634136	0.02835086	-0.02932421
S3	0.03360562	3.46629748	-0.02932221
S4	3.47436421	3.46910119	0.04155284
S5	3.50611594	0.05168506	-3.43448486
S6	0.05699815	3.50603860	-3.43448284
Br1	1.80699594	1.80426377	-6.17716212
Br2	1.76557771	6.22257955	-1.64057430
Br3	1.76502494	-2.69732009	-1.72319310
Br4	1.72422273	1.72161082	2.74697861
Br5	6.22524646	1.75614105	-1.64057690
Br6	-2.69464381	1.76911841	-1.72319050
Br7	-0.09251367	-0.09236821	-3.70512305
Br8	3.66000353	3.65446129	-3.63561558
Re1	1.75383926	3.64096998	-1.68422762
Re2	3.64362203	1.74831854	-1.68422872
Re3	1.74824134	1.74559453	0.15742745
Re4	1.77712755	-0.11534689	-1.71880160
Re5	-0.11265522	1.77730456	-1.71880049
Re6	1.78294062	1.78024340	-3.58365334

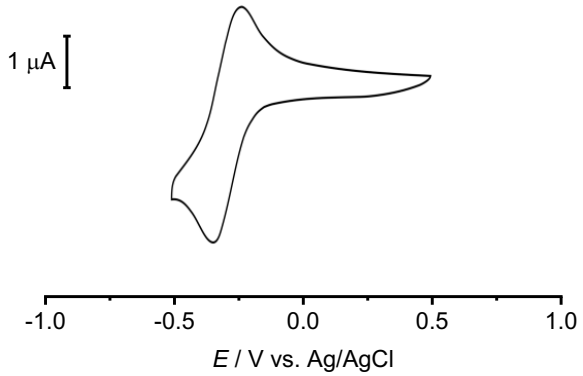

Figure S1. Cyclic Voltammogram of $[Tc_6(\mu_3\text{-}S)_2(\mu_3\text{-}Br)_2Br_6]^{2-}$ in 0.1 M Bu_4NPF_6-CH_3CN. Working electrode is 1 mm diameter of glassy carbon disk.

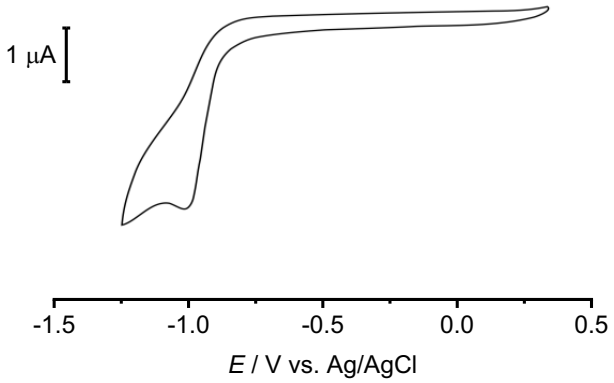

Figure S2. Cyclic Voltammogram of $[Tc_6(\mu_3\text{-}S)_7(\mu_3\text{-}Br)Br_6]^{3-}$ in 0.1 M Bu_4NPF_6-CH_3CN. Working electrode is 1 mm diameter of glassy carbon disk.

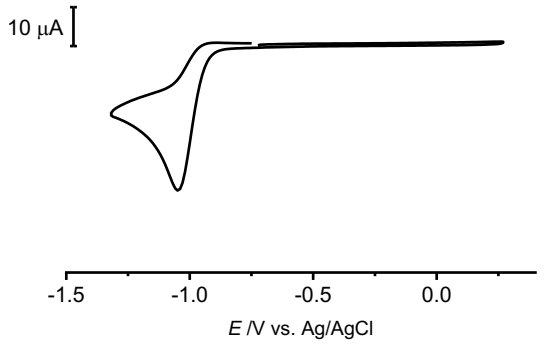

Figure S3. Cyclic Voltammogram of $[Re_6(\mu_3\text{-}S)_6(\mu_3\text{-}Br)_2Br_6]^{2-}$ in 0.1 M Bu_4NPF_6-CH_3CN. Working electrode is 3 mm diameter of glassy carbon disk.

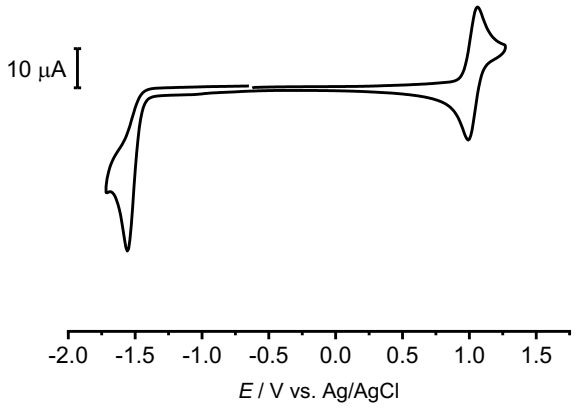

Figure S4. Cyclic Voltammogram of $[Re_6(\mu_3\text{-}S)_7(\mu_3\text{-}Br)Br_6]^{3-}$ in 0.1 M Bu_4NPF_6-CH_3CN. Working electrode is 3 mm diameter of glassy carbon disk.

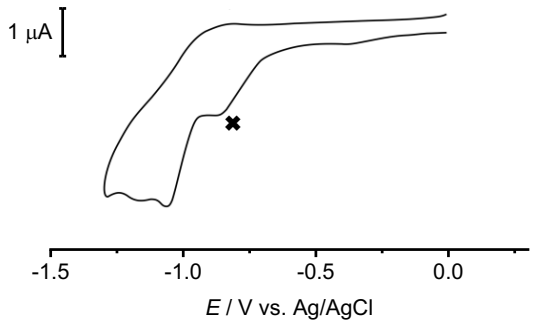

Figure S5. Cyclic Voltammogram of $[Tc_6(\mu_3\text{-}S)_7(\mu_3\text{-}Cl)Cl_6]^{3-}$ in 0.1 M Bu_4NPF_6-CH_3CN. Working electrode is 1 mm diameter of glassy carbon disk.

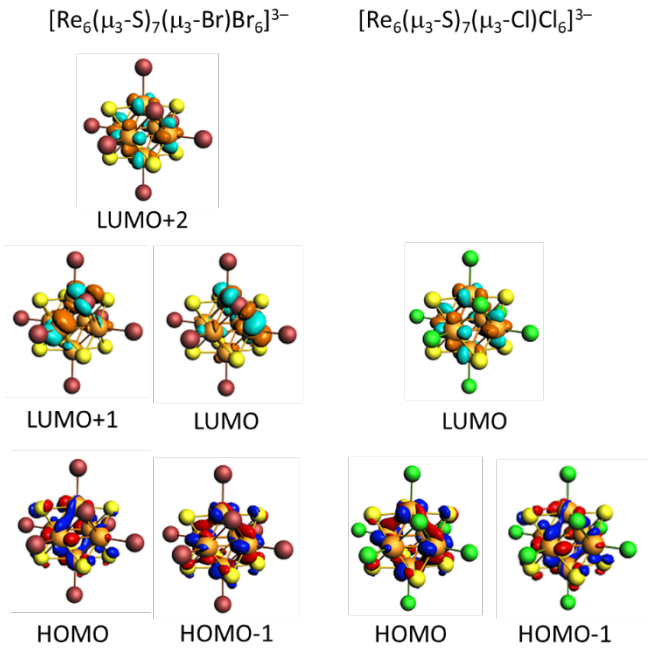

Figure S6. Contour plots of near the frontier orbital levels of $[Re_6(\mu_3\text{-}S)_7(\mu_3\text{-}X)X_6]^{3-}$ (X = Br, Cl; Re, orange; S, yellow; Br, brown; Cl, green; isovalue = 0.04).

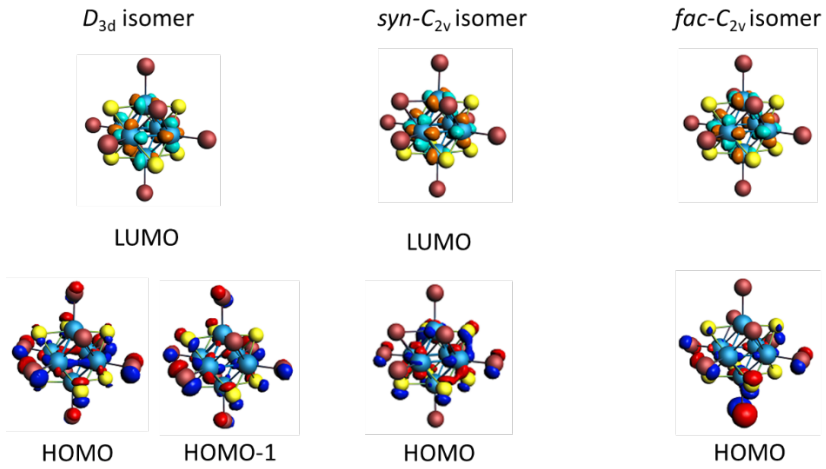

Figure S7. Contour plots of near the frontier orbital levels of three isomers for $[Tc_6(\mu_3\text{-}S)_6(\mu_3\text{-}Br)_2Br_6]^{2-}$ (Tc, skyblue; S, yellow; Br, brown; isovalue = 0.04).

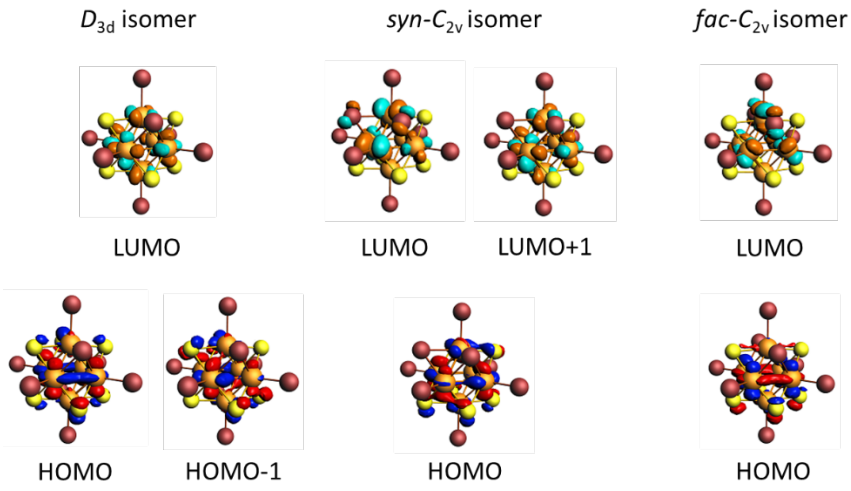

Figure S8. Contour plots of near the frontier orbital levels of three isomers for $[Re_6(\mu_3\text{-}S)_6(\mu_3\text{-}Br)_2Br_6]^{2-}$ (Re, orange; S, yellow; Br, brown; isovalue = 0.04).

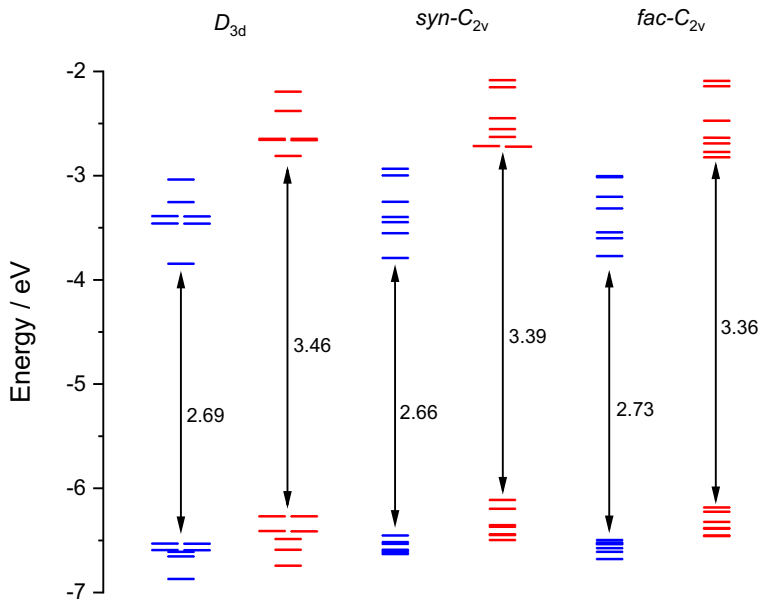

Figure S9. Energy diagrams near the HOMO/LUMO levels of three isomers for $[Tc_6(\mu_3\text{-}S)_6(\mu_3\text{-}Br)_2Br_6]^{2-}$ (blue) and those of $[Re_6(\mu_3\text{-}S)_6(\mu_3\text{-}Br)_2Br_6]^{2-}$ (red).

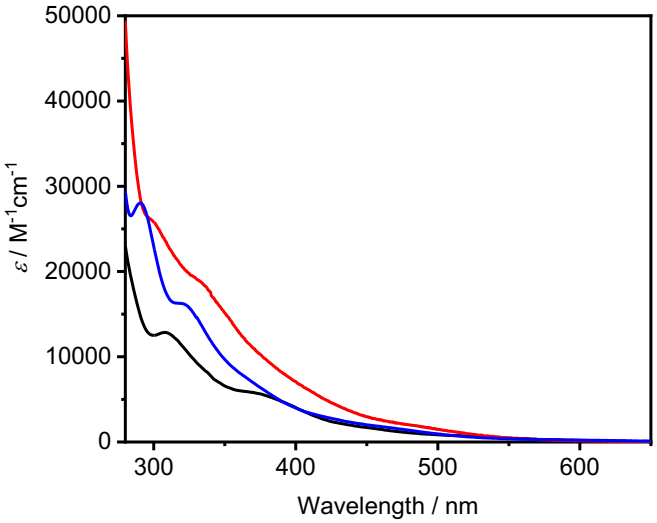

Figure S10. UV-vis spectra for $(PPh_4)_2[Tc_6(\mu_3\text{-}S)_6(\mu_3\text{-}Br)_2Br_6]$ (black), $(PPh_4)_3[Tc_6(\mu_3\text{-}S)_7\mu_3\text{-}Br)Br_6]$ (red), and $(PPh_4)_2[Tc_6(\mu_3\text{-}S)_7(\mu_3\text{-}Br)_2Br_6]$ (blue) in CH_3CN.

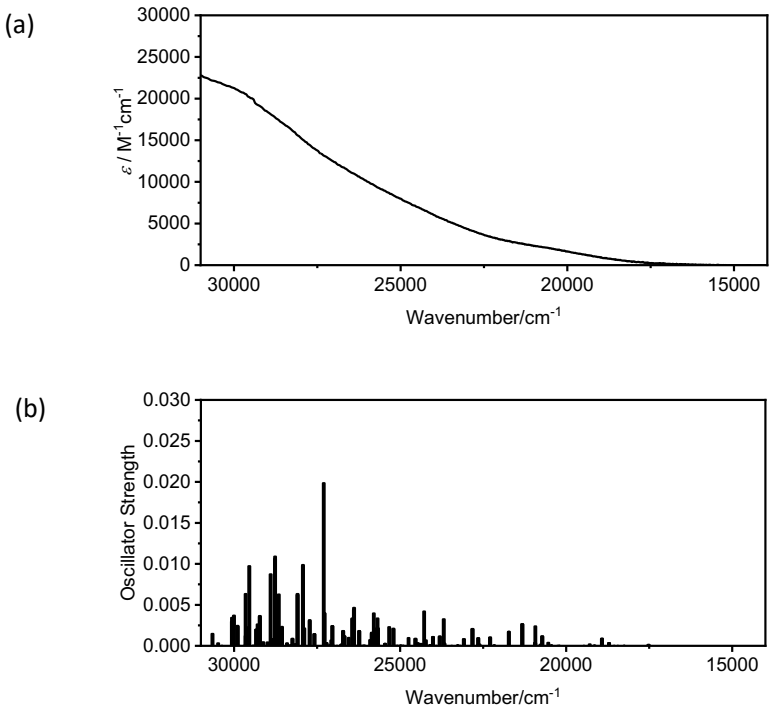

Figure S11. (a) Experimental UV-vis spectrum for $(PPh_4)_3[Tc_6(\mu_3\text{-}S)_7(\mu_3\text{-}Br)Br_6]$ in CH_3CN and (b) calculated electronic transitions for $[Tc_6(\mu_3\text{-}S)_7(\mu_3\text{-}Br)Br_6]^{3-}$ in CH_3CN.

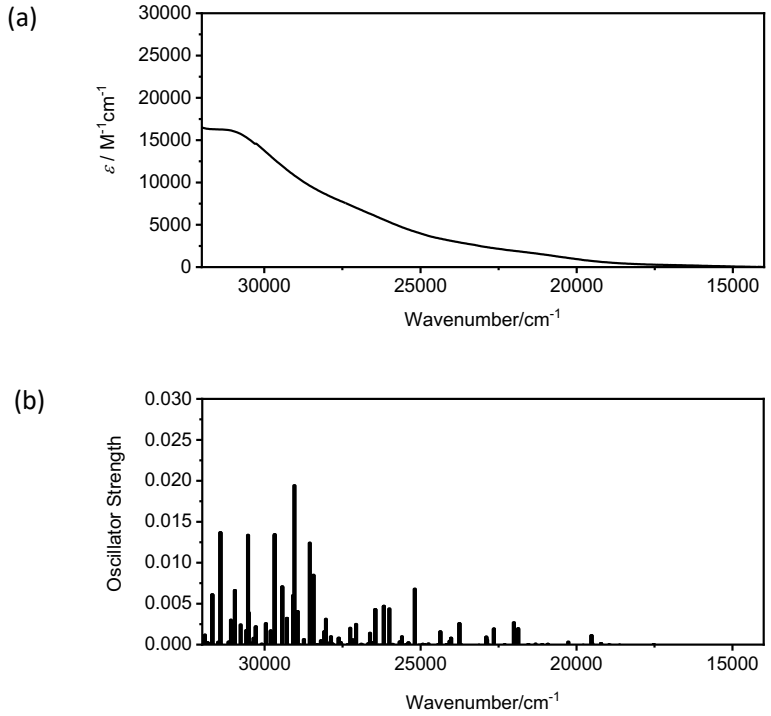

Figure S12. (a) Experimental UV-vis spectrum for $(PPh_4)_3[Tc_6(\mu_3\text{-}S)_7(\mu_3\text{-}Cl)Cl_6]$ in CH_3CN and (b) calculated electronic transitions for $[Tc_6(\mu_3\text{-}S)_7(\mu_3\text{-}Cl)Cl_6]^{3-}$ in CH_3CN.

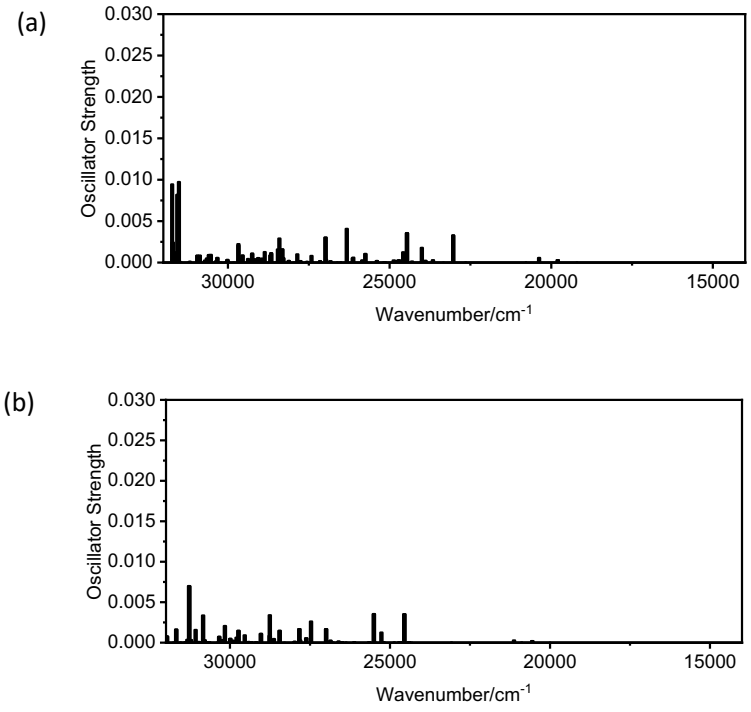

Figure S13. (a) calculated electronic transitions for $[Re_6(\mu_3\text{-}S)_7(\mu_3\text{-}Br)Br_6]^{3-}$ in CH_3CN and (b) calculated electronic transitions for $[Re_6(\mu_3\text{-}S)_7(\mu_3\text{-}Cl)Cl_6]^{3-}$ in CH_3CN.

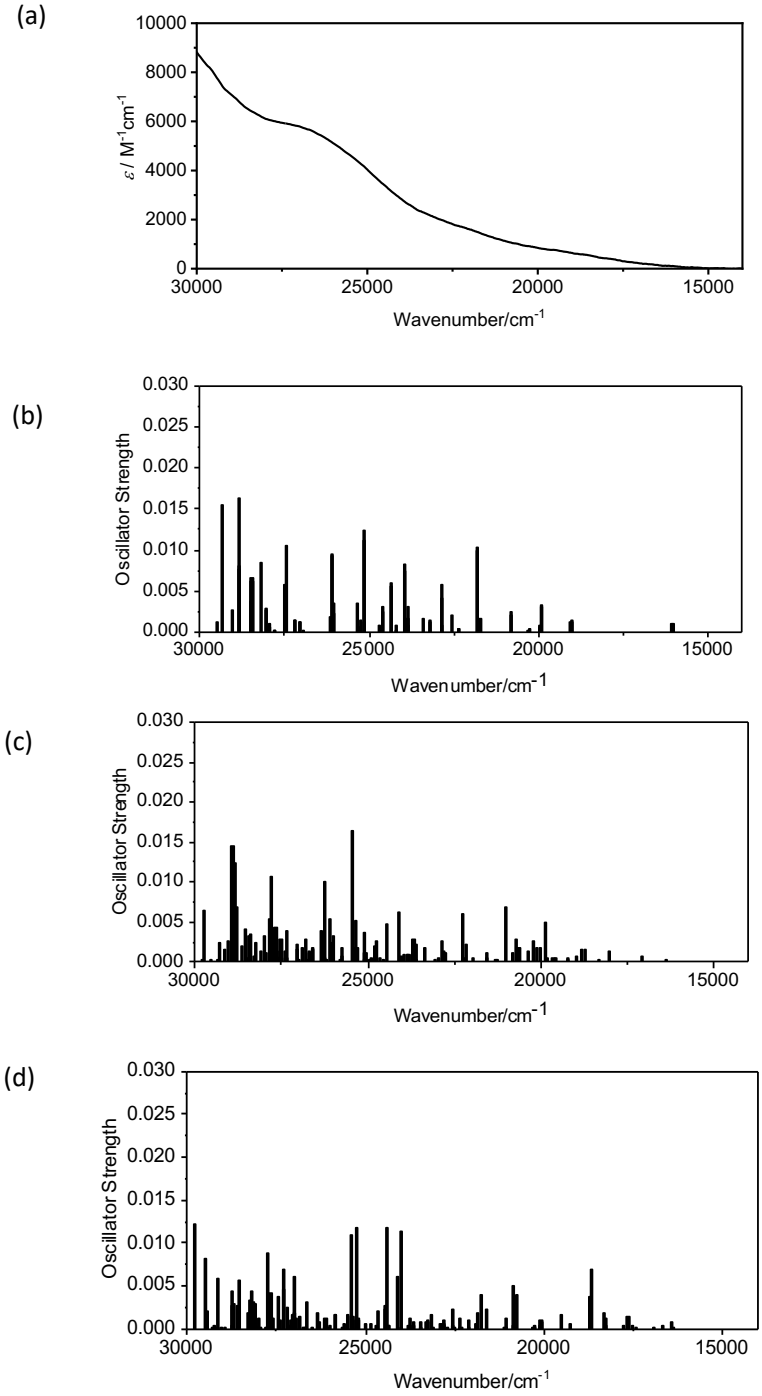

Figure S14. (a) Experimental UV-vis spectrum for $(PPh_4)_2[Tc_6(\mu_3\text{-}S)_6(\mu_3\text{-}Br)_2Br_6]$ in CH_3CN and (b-d) calculated electronic transitions for $[Tc_6(\mu_3\text{-}S)_6(\mu_3\text{-}Br)_2Br_6]^{2-}$ in CH_3CN [(b) D_{3d} isomer; (c) *syn*-C_{2v} isomer, and (d) *fac*-C_{2v} isomer].

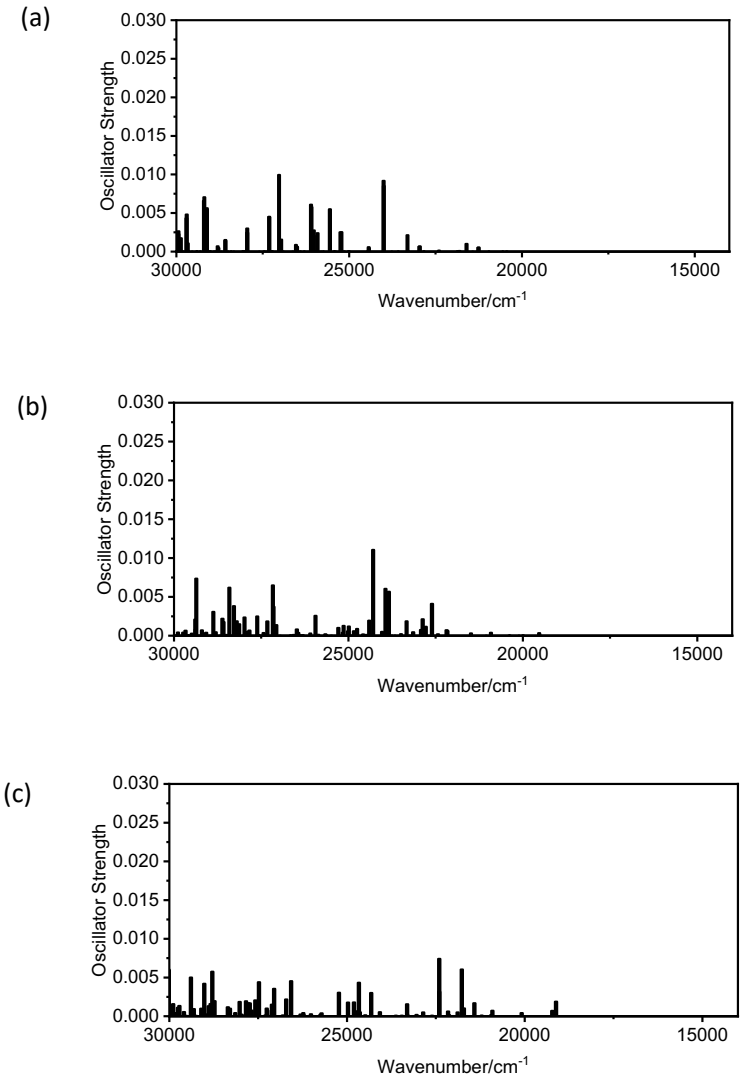

Figure S15. Calculated electronic transitions for $[Re_6(\mu_3\text{-}S)_6(\mu_3\text{-}Br)_2Br_6]^{2-}$ in CH_3CN [(a) D_{3d} isomer; (b) *syn*-C_{2v} isomer, and (c) *fac*-C_{2v} isomer].