Supporting Information for

Spectroscopic, Theoretical and Photophysical Study of the Excited-State Attributes of Hexanuclear Rhenium(III) Chalcogenide Clusters $[Re_6(\mu_3\text{-}Q)_8]^{2+}$ (Q = S, Se)

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Table S1. Mulliken gross populations of frontier and near-frontier orbitals in ground-state $[Re_6S_8Cl_6]^{4-}$ (**1**) as calculated with the Hay-Wadt effective core potentials and basis set. Extended Hückel results are included for comparison.

MO Number	Energy (eV)	Symmetry	Re	S_8	Cl_6
Hartree-Fock		*HOMO–LUMO gap: 7.93 eV*			
97-99	11.03	t_{1u}	81.2	18.8	0.0
94-96	10.91	t_{1g}	82.2	16.9	1.0
93 (LUMO)	10.03	a_{2g}	100	0.0	0.0
91-92 (HOMOs)	2.10	e_g	64.8	34.8	0.5
88-90	1.54	a_1	15.0	64.3	20.7
85-87	1.48	t_{1g}	18	68.5	13.4
82-84	1.09	t_{1u}	38.7	24.4	36.9
79-81	0.76	t_{2u}	34.5	43.4	22.1
76-78	–0.23	t_{1u}	43.9	32.4	23.7
75	–0.39	a_{1g}	20.5	3.8	75.6
BLYP		*HOMO–LUMO gap: 2.19 eV*			
97-99	8.44	t_{1u}	69.3	19.1	11.6
94-96	8.40	t_{1g}	84.6	13.1	2.3
93 (LUMO)	8.07	a_{2g}	100	0.0	0.0
91-92 (HOMOs)	5.88	e_g	71.8	28.2	0.0
88-90	5.41	t_{2u}	41.1	18.9	40.0
85-87	5.39	t_{1g}	8.1	62.6	29.3
82-84	5.21	t_{1u}	23.7	51.6	24.6
79-81	5.02	t_{2g}	33.9	23.7	42.4
76-78	4.37	t_{1u}	11.0	28.0	60.9
Becke3LYP		*HOMO–LUMO gap: 3.41 eV*			
97-99	8.89	t_{1u}	69.9	19.0	11.1
94-96	8.71	t_{1g}	83.8	14.2	2.0
93 (LUMO)	8.29	a_{2g}	100	0.0	0.0
91-92 (HOMOs)	4.88	e_g	70.3	29.7	0.0
88-90	4.39	t_{1g}	9.7	63.6	26.7
85-87	4.32	t_{2u}	40.1	20.3	39.6
82-84	4.25	t_{1u}	22.0	57.9	20.1
79-81	3.93	t_{2g}	34.2	29.3	36.5
76-78	3.16	t_{1u}	16.9	26.3	56.8

Table S1 (continued)

MO Number	Energy (eV)	Symmetry	Re	S_8	Cl_6
Extended Hückel					
36-39		t_{2u}	80	19	1
39-41		t_{1g}	80	17	3
42 (LUMO)		a_{2g}	100	0	0
43-44 (HOMOs)		e_g	78	22	0
45-47		t_{2u}	71	11	18
48-50		t_{1u}	38	46	16
51-53		t_{2g}	65	20	15
54-56		t_{1g}	10	61	29
57		a_{1g}	56	1	43

Table S2. Mulliken gross populations of frontier and near-frontier orbitals in ground-state $[Re_6S_8Br_6]^{4-}$ (**2**) as calculated with the Hay-Wadt effective core potentials and basis set. Extended Hückel results are included for comparison

MO Number	Energy (eV)	Symmetry	Re	S_8	Br_6
Hartree-Fock		*HOMO–LUMO gap: 7.92 eV*			
97-99	10.82	t_{2u}	80.6	19.4	–0.1
94-96	10.64	t_{1g}	81.4	17.8	0.8
93 (LUMO)	9.82	a_{2g}	100	0.0	0.0
91-92 (HOMOs)	1.9	e_g	65.4	33.3	1.3
88-90	1.47	t_{1g}	12.4	51.7	35.9
85-97	1.38	t_{1u}	17.3	59.4	23.3
82-84	1.17	t_{2u}	26.2	17.4	56.4
79-81	0.75	t_{2g}	21.4	25.6	53.0
78	0.06	a_{1g}	19.0	2.8	78.3
75-77	0.04	t_{1u}	6.9	13.2	79.9
BLYP		*HOMO–LUMO gap: 2.30 eV*			
97-99	8.33	t_{1g}	83.6	14.4	1.9
94-96	8.28	t_{1u}	66.5	18.7	14.8
93 (LUMO)	8.03	a_{2g}	100	0.0	0.0
91-92 (HOMOs)	5.73	e_g	71.9	28.0	0.1
88-90	5.31	t_{2u}	33.0	15.4	51.7
85-87	5.29	t_{1g}	7.5	52.2	40.3
82-84	5.10	t_{1u}	20.6	46.1	33.3
79-81	4.92	t_{2g}	23.1	16.4	60.4
76-78	4.42	t_{1u}	6.2	23.9	69.8
Becke3LYP		*HOMO–LUMO gap: 3.40 eV*			
97-99	8.48	t_{1u}	67.1	18.2	14.7
94-96	8.41	t_{1g}	83.0	15.4	1.6
93 (LUMO)	8.03	a_{2g}	100	0.0	0.0
91-92 (HOMOs)	4.63	e_g	70.9	28.9	0.2
88-90	4.21	t_{1g}	8.8	51.9	39.3
85-87	4.17	t_{2u}	31.1	15.9	53.0
82-84	4.06	t_{1u}	19.9	50.8	29.3
79-81	3.78	t_{2g}	22.8	19.0	58.2
76-78	3.24	t_{1u}	6.2	20.2	73.6

Table S2 (continued)

MO Number	Energy (eV)	Symmetry	Re	S_8	Br_6
Extended Hückel					
36-38		t_{2u}	79	19	2
39-41		t_{1g}	79	16	5
42		a_{2g}	100	0	0
43-44		e_g	77	23	0
45-47		t_{2u}	45	12	43
48-50		t_{1u}	29	23	48
51-53		t_{2g}	40	11	49
54-56		t_{1g}	2	39	59
57		a_{1g}	40	1	59

Table S3. Mulliken gross populations of frontier and near-frontier orbitals in ground-state $[Re_6S_8I_6]^{4-}$ (**3**) as calculated with the Hay-Wadt effective core potentials and basis set. Extended Hückel results are included for comparison.

MO Number	Energy (eV)	Symmetry	Re	S_8	I_6
Hartree-Fock		*HOMO–LUMO gap: 7.87 eV*			
97-99	10.63	t_{2u}	80.4	19.8	–0.2
94-96	10.4	t_{1g}	80.7	18.6	0.6
93 (LUMO)	9.60	a_{2g}	100	0.0	0.0
91-92 (HOMOs)	1.73	e_g	65.8	31.3	2.9
88-90	1.53	t_{1u}	8.5	34.8	56.7
85-87	1.38	t_{2u}	15.4	10.9	73.7
82-84	1.37	t_{1u}	15.2	43.6	41.1
79-81	0.99	t_{2g}	8.1	8.3	83.6
76-78	0.52	t_{1u}	7.0	17.3	75.8
BLYP		*HOMO–LUMO gap: 2.17 eV*			
97-99	7.72	t_{1g}	83.6	14.9	1.5
94-96	7.58	t_{1u}	65.6	17.0	17.5
93 (LUMO)	7.46	a_{2g}	100	0.0	0.0
91-92(HOMOs)	5.29	e_g	72.9	26.8	0.3
88-90	4.95	t_{2u}	25.0	11.5	63.5
85-87	4.92	t_{1g}	6.6	39.1	54.3
82-84	4.75	t_{1u}	17.0	36.3	46.8
79-81	4.63	t_{2g}	13.2	8.8	78.0
76-78	4.29	t_{1u}	7.9	26.3	65.8
Becke3LYP		*HOMO–LUMO gap: 3.38 eV*			
97-99	8.1	t_{1g}	82.6	16.1	1.3
94-96	8.05	t_{2u}	65	17	18
93(LUMO)	7.74	a_{2g}	100	0.0	0.0
91-92(HOMOs)	4.36	e_g	71.8	27.7	0.4
88-90	4.04	t_{2g}	7.1	39.2	53.7
85-87	4.02	t_{2u}	22.5	11.7	65.8
82-84	3.88	t_{1u}	17.1	41.2	41.7
79-81	3.68	t_{2g}	12.6	9.8	77.6
76-78	3.29	t_{1u}	7	22.4	70.6
75	2.99	a_{1g}	16.6	1.4	82

Table S3 (continued)

MO Number	Energy (eV)	Symmetry	Re	S_8	I_6
Extended Hückel					
36-38		t_{2u}	79	21	0
39-41		t_{1g}	78	20	2
42		a_{2g}	100	0	0
43-44		e_g	77	23	0
45-47		t_{2u}	31	7	62
48-50		t_{1u}	18	15	67
51-53		t_{2g}	22	6	72
54		a_{1g}	26	1	73

Table S4. Mulliken gross populations of frontier and near-frontier orbitals in ground-state $[Re_6S_8(CN)_6]^{4-}$ (**13**) as calculated with the Hay-Wadt effective core potentials and basis set. Extended Hückel results are included for comparison.

MO Number	Energy (eV)	Symmetry	Re	S_8	$(CN)_6$
Hartree-Fock		*HOMO–LUMO gap: 8.07 eV*			
115-117	10.66	t_{2u}	79.4	18.8	20.6
112-114	10.29	t_{1g}	74.8	18.3	25.2
111 (LUMO)	9.84	a_{2g}	100	0.0	0.0
109-110 (HOMOs)	1.77	e_g	64.5	34.2	35.5
106-108	0.95	t_{1u}	22.9	70.0	77.1
103-105	0.69	t_{1g}	23.7	67.6	76.3
100-102	0.27	t_{2u}	59.6	23.6	40.4
97-99	0.16	t_{2g}	45.4	46.6	54.5
94-96	–0.6	t_{2u}	51.8	39.6	48.2
92-93	–1.21	e_u	47.2	52.8	52.8
BLYP		*HOMO–LUMO gap: 2.19 eV*			
115-117	8.00	t_{2u}	73.5	21.4	5.1
114	7.6	a_{2g}	100	0.0	0.0
111-113 (LUMOs)	7.55	t_{1g}	69.9	16.4	13.7
109-110 (HOMOs)	5.36	e_g	71.4	27.9	0.7
106-108	4.69	t_{1u}	32	53.9	14.1
103-105	4.54	t_{1g}	64	16.9	19.2
100-102	4.48	t_{2u}	15.3	70.9	13.8
97-99	4.27	t_{2g}	53.4	31.9	14.7
96	3.9	a_{1g}	30	2.6	67.4
Extended Hückel					
52-53		e_u	61	39	0
54-56		t_{2u}	73	23	4
57-59		t_{1g}	66	24	10
60 (LUMO)		a_{2g}	100	0	0
61 (HOMO)		a_{1g}	41	1	58
62-63		e_g	78	22	0
64-66		t_{1u}	36	43	21
67-69		t_{2u}	89	5	6
70-72		t_{1g}	67	29	4
73-74		e_g	23	0	77

The Becke3LYP calculation did not converge to an energy minimum, and is excluded.

Table S5. Observed and calculated vibrational frequencies (cm^{-1}) of $[Re_6S_8Cl_6]^{4-}$ (**1**) using the Hay-Wadt effective core potentials and the enhanced basis set. Raman-active modes are in bold type.

Mode	Hartree-Fock	Becke3LYP	Experimental
T_{2u}	90.53	81.67	
T_{2g}	**101.63**	**92.20**	not observed[a]
T_{1u}	105.79	95.82	
T_{1g}	132.27	118.93	
E_g	**172.16**	**158.95**	**162**
T_{2u}	205.42	188.40	
T_{1u}	208.70	196.56	
A_{1g}	**215.64**	**199.84**	**222**
T_{2g}	**242.10**	**214.44**	not observed
E_g	**243.91**	**226.01**	not observed
T_{1u}	266.23	241.80	
E_u	268.16	244.18	
E_g	**301.65**	**277.72**	**291**
T_{2g}	**301.68**	**270.72**	**277**
T_{1g}	306.84	270.00	
T_{2u}	312.22	276.15	
A_{1g}	**322.34**	**284.55**	**304**
T_{1u}	338.91	301.56	
A_{2u}	420.12	384.05	
T_{2g}	**425.27**	**386.31**	**395**
T_{1u}	437.73	396.85	
A_{1g}	**462.83**	**415.55**	**428**
RMS dev.[b]	12.9	–15.3	
Avg. dev.[b]	21.5	18.3	

[a] Instrumental cutoff was 100 cm^{-1}. [b] Excluding C≡N vibrations.

Table S6. Observed and calculated vibrational frequencies (cm^{-1}) of $[Re_6S_8(CN)_6]^{4-}$ (**13**) using the Hay-Wadt effective core potentials and the enhanced basis set. Raman-active modes are in bold type.

Mode	Hartree-Fock	Becke3LYP	Experimental
T_{2u}	85.30	75.41	
T_{2g}	**93.79**	**83.70**	not observed[a]
T_{1u}	95.63	85.15	
T_{1g}	112.47	99.01	
E_g	**185.49**	**166.71**	**167**
T_{2u}	192.20	175.09	
T_{2g}	**236.21**	**208.17**	
T_{1u}	248.25	222.79	
E_u	263.77	241.18	
A_{1g} Re_6 ReC (s)	**281.25**	**244.24**	**245**
E_g	**295.45**	**273.71**	**280**
T_{2g}	**300.17**	**269.95**	**280**
T_{1g}	307.38	270.11	
T_{2u}	315.09	279.40	
T_{1u}	321.26	288.72	
E_g	**371.53**	**362.89**	**368**
T_{1u}	377.38	364.14	
A_{1g} Re_6 ReC (a)	**386.24**	**370.51**	**397**
T_{2g}	**402.82**	**368.57**	**417**
T_{1u}	410.88	374.63	
A_{2u}	412.19	378.68	
T_{1g}	425.95	380.03	
T_{2u}	439.65	396.88	
A_{1g} (S_8)	**452.40**	**410.33**	**431**
T_{1u}	455.61	408.96	
T_{2g}	**461.79**	**414.73**	not observed
E_g	**2433.32**	**2191.93**	**2120**
T_{1u}	2433.67	2192.19	
A_{1g} (CN)	**2435.29**	**2193.86**	**2120**
RMS dev.[b]	19.6	21.3	
Avg. dev.[b]	11.3	–14.8	

[a] Instrumental cutoff was 100 cm^{-1}. [b] Excluding C≡N vibrations

Figure S1. A band-shape deconvolution of the luminescence profile of crystalline **1** at 290 K.

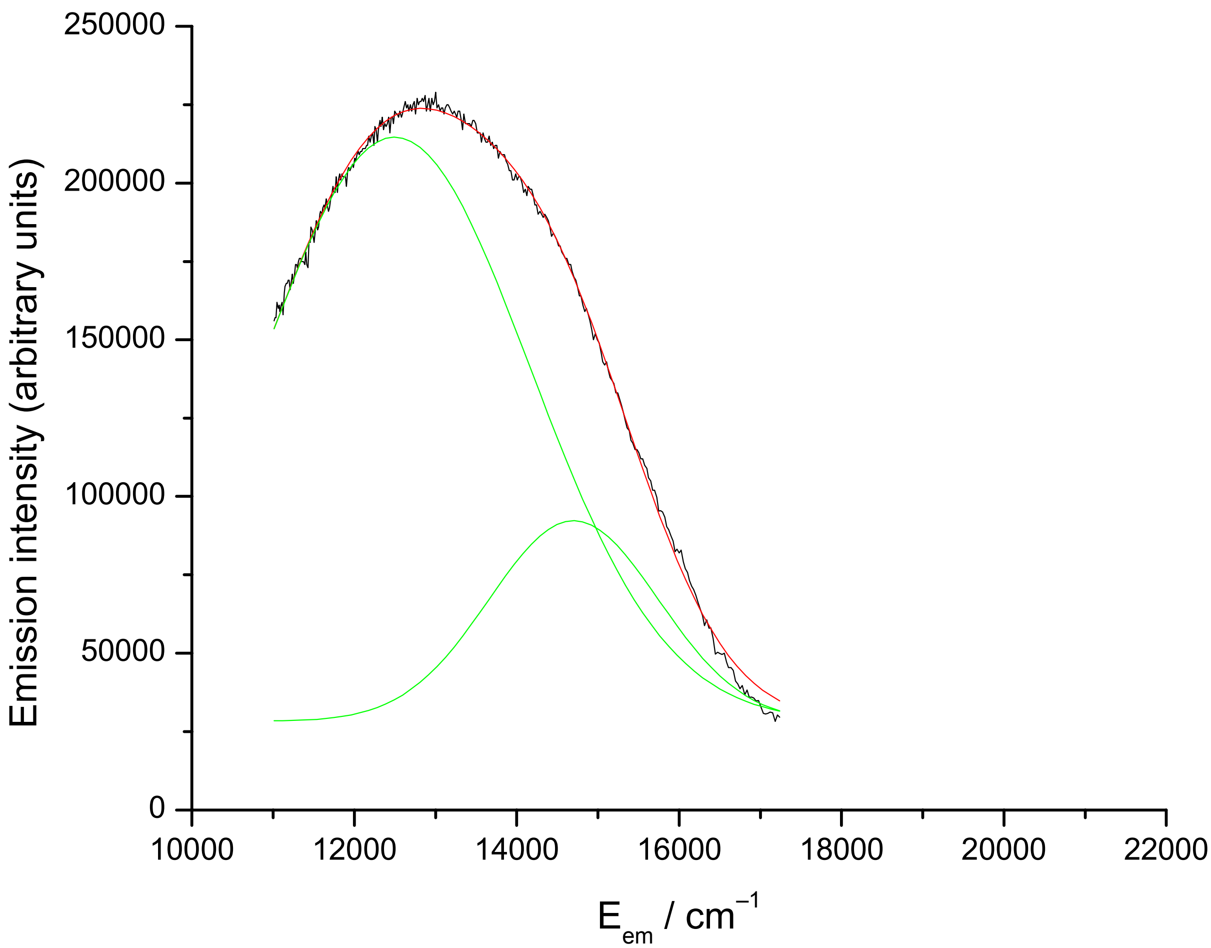

Figure S2. Raman spectra of $[Re_6S_8(PEt_3)_5Br]Br$ (**6**) where polarization of scattered light is parallel (∥) and perpendicular (⊥) to the incident irradiation.

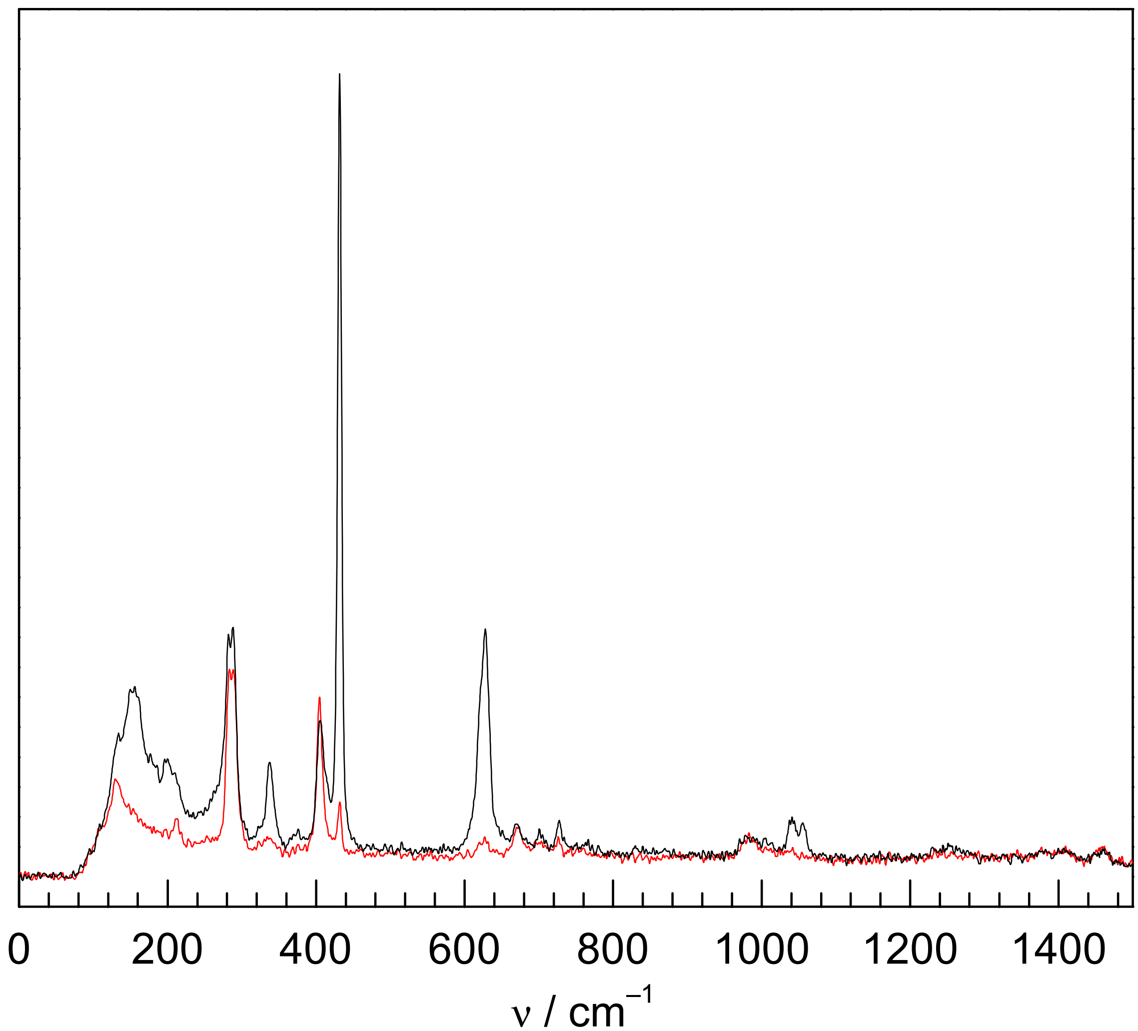

Figure S3. Raman spectra of *trans*-[$Re_6S_8(PEt_3)_4Br_2$] (**7**) where polarization of scattered light is parallel (ǁ) and perpendicular (⊥) to the incident irradiation.

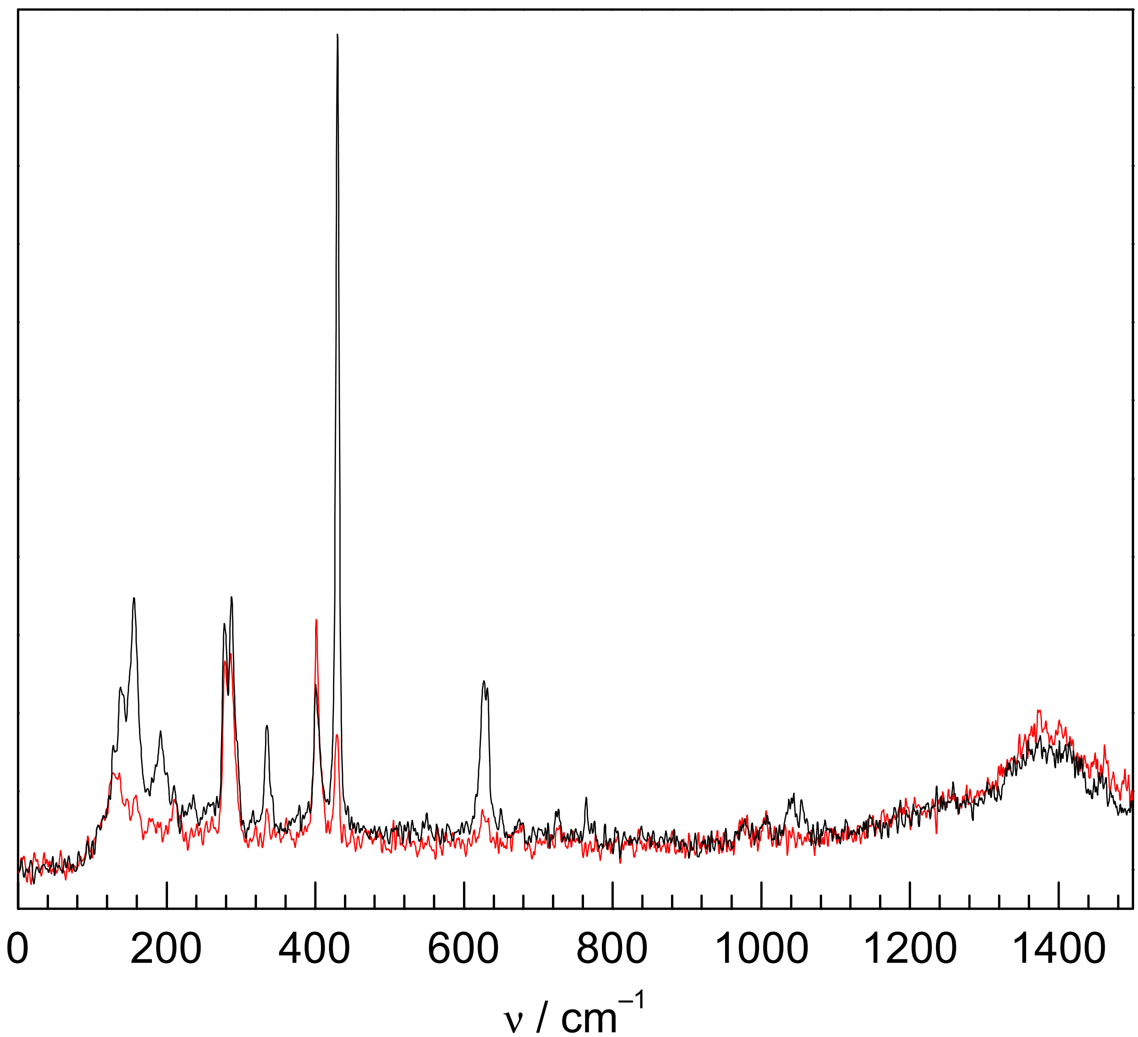

Figure S4. Raman spectra of *cis*-$[Re_6S_8(PEt_3)_4Br_2]$ (**8**) where polarization of scattered light is parallel (∥) and perpendicular (⊥) to the incident irradiation.

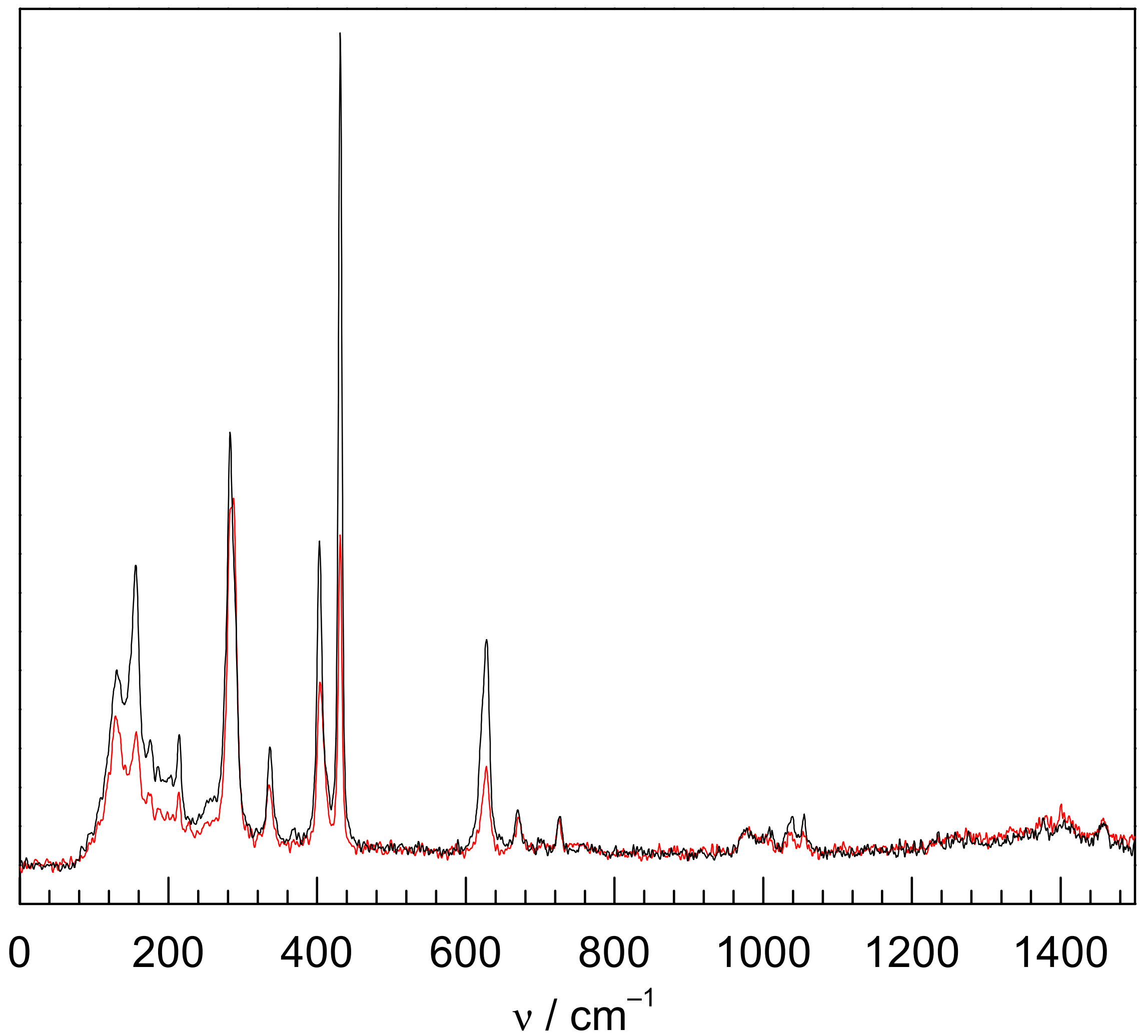

Figure S5. Raman spectra of (Bu_4N)*mer*-$[Re_6S_8(PEt_3)_3Br_3]$ (**9**) where polarization of scattered light is parallel (∥) and perpendicular (⊥) to the incident irradiation.