Electronic Supplementary Information

for **Molecular heterometallic clusters $[Re_{6-x}Mo_xS_8L_6]$ (x=2-3, L = py, etpy, tbp): negligible influence of the x value on the crystal structures**

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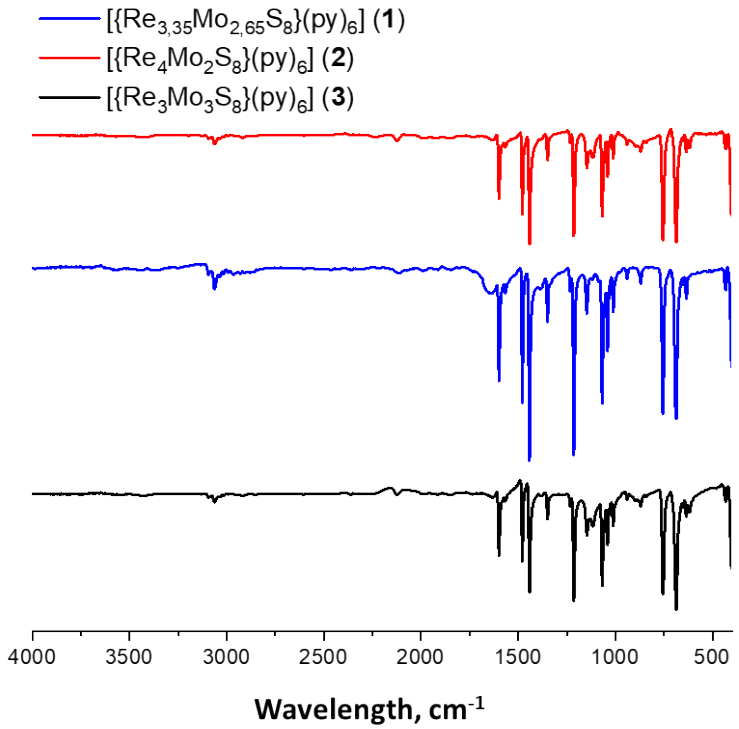

Figure S1. IR spectra for compounds **1-3**.

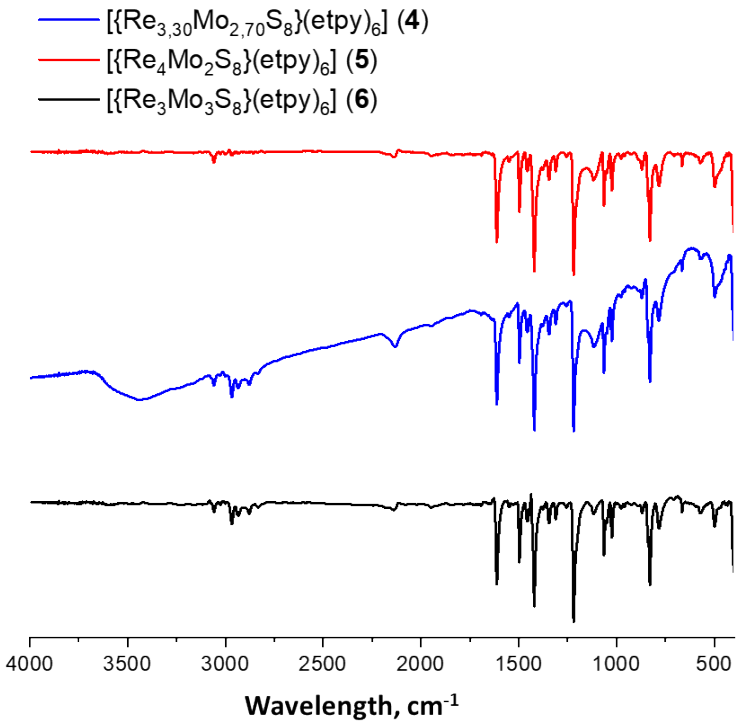

Figure S2. IR spectra for compounds (**4-6**).

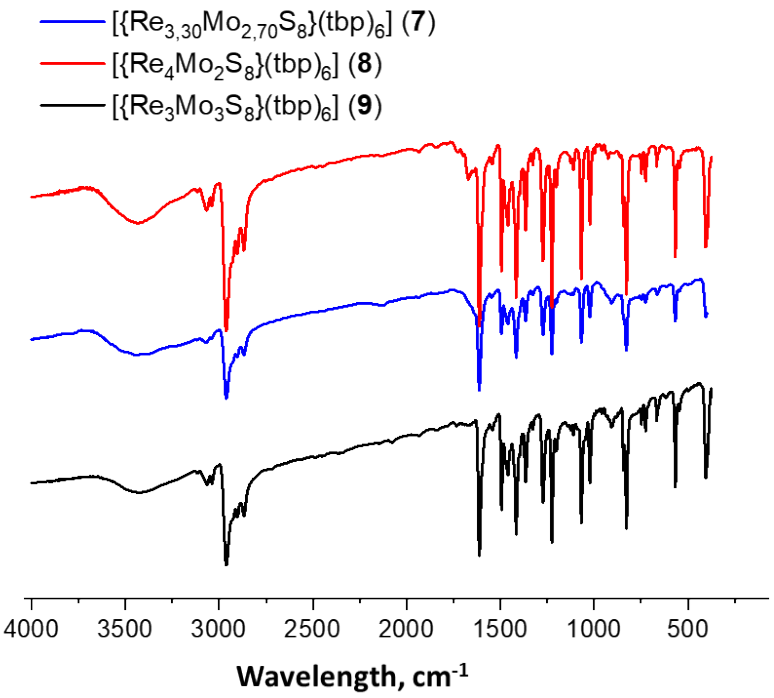

Figure S3. IR spectra for compounds (**7-9**).

Table S1. Crystallographic data and details of the structure refinements for the compounds **1**–**3**.

	1	**2**	**3**
Chemical formula	$C_{30}H_{30}N_6Re_{3.35}Mo_{2.65}S_8$	$C_{30}H_{30}N_6Re_4Mo_2S_8$	$C_{30}H_{30}N_6Re_3Mo_3S_8$
Molecular weight, g/mol	1609.09	1667.76	1577.50
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a, Å	9.3458(4)	9.3333(2)	9.3362(8)
b, Å	10.5903(4)	10.5520(2)	10.5758(8)
c, Å	11.8441(5)	11.8701(2)	11.8771(9)
α, °	114.4320(10)	114.4530(10)	114.524(2)
β, °	90.7490(10)	91.1010(10)	91.007(3)
γ, °	109.1920(10)	108.9960(10)	109.100(3)
V, Å^3	992.72(7)	989.99(3)	992.01(14)
Z	1	1	1
$\rho_{calcd.}$, g·cm^{-3}	2.692	2.797	2.641
μ, mm^{-1}	11.436	13.246	10.488
θ range, °	2.23 – 26.39	2.28 – 30.49	2.60 – 29.55
Miller indices range	-11 ≤ h ≤ 9 -12 ≤ k ≤ 13 -14 ≤ l ≤ 14	-12 ≤ h ≤ 13 -15 ≤ k ≤ 15 -16 ≤ l ≤ 16	-12 ≤ h ≤ 12 -14 ≤ k ≤ 14 -16 ≤ l ≤ 14
Reflections collected/unique	10546/4061	15877/5997	15390/5504
Reflections (I>2σ(I))	3615	5315	5133
R_{int}	0.0218	0.0297	0.0273
GoF	1.044	1.023	1.059
R_1 / wR_2(I> 2σ(I))	R_1 = 0.0195 wR_2 = 0.0402	R_1 = 0.0274 wR_2 = 0.0493	R_1 = 0.0217 wR_2 = 0.0479
R_1 / wR_1 (all data)	R_1 = 0.0240 wR_2 = 0.0418	R_1 = 0.0324 wR_2 = 0.0515	R_1 = 0.0239 wR_2 = 0.0488
$\Delta\rho_{max}/\Delta\rho_{min}$ (e·Å^3)	0.842/-0.655	1.077/-1.110	1.115/-1.063

Table S2. Crystallographic data and details of the structure refinements for the compounds **4**–**6**.

	4	**5**	**6**
Chemical formula	$C_{42}H_{54}N_6Re_{3.3}Mo_{2.7}S_8$	$C_{42}H_{54}N_6Re_4Mo_2S_8$	$C_{42}H_{54}N_6Re_3Mo_3S_8$
Molecular weight, g/mol	1772.89	1836.07	1745.81
Space group	$I4_1/a$	$I4_1/a$	$I4_1/a$
a, Å	14.2868(2)	14.2615(4)	14.2677(11)
b, Å	14.2868(2)	14.2615(4)	14.2677(11)
c, Å	24.4236(8)	24.4091(10)	24.4726(4)
α, °	90	90	90
β, °	90	90	90
γ, °	90	90	90
V, Å^3	4985.2(2)	4964.6(3)	4981.8(10)
Z	4	4	4
$\rho_{calcd.}$, g·cm^{-3}	2.362	2.456	2.328
μ, mm^{-1}	9.012	10.578	8.366
θ range, °	2.62 – 28.68	2.62 – 31.42	2.62 – 29.50
Miller indices range	-8 ≤ h ≤ 19 -18 ≤ k ≤ 7 -30 ≤ l ≤ 20	-20 ≤ h ≤ 20 -20 ≤ k ≤ 20 -35 ≤ l ≤ 35	-19 ≤ h ≤ 19 -19 ≤ k ≤ 18 -22 ≤ l ≤ 33
Reflections collected/unique	6112/3043	120331/4144	16324/3483
Reflections (I>2σ(I))	2304	2933	2378
R_{int}	0.017	0.0757	0.0445
GoF	1.060	1.055	1.033
R_1 / wR_2(I> 2σ(I))	R_1 = 0.0189 wR_2 = 0.0363	R_1 = 0.0218 wR_2 = 0.0400	R_1 = 0.0245 wR_2 = 0.0456
R_1 / wR_1 (all data)	R_1 = 0.0301 wR_2 = 0.0390	R_1 = 0.0414 wR_2 = 0.0445	R_1 = 0.0417 wR_2 = 0.0516
$\Delta\rho_{max}/\Delta\rho_{min}$ (e·Å^3)	0.735/-0.635	0.968/-1.603	0.529/-0.522

Table S3. Crystallographic data and details of the structure refinements for the compounds **7**–**9**.

	7	**8**	**9**
Chemical formula	$C_{54}H_{78}N_6Re_{3.30}Mo_{2.70}S_8$	$C_{59.188}H_{85.782}N_{8.594}Re_4Mo_2S_8$	$C_{59.168}H_{85.752}N_{8.584}Re_3Mo_3S_8$
Molecular weight, g/mol	1941.20	2110.91	2020.18
Space group	$P4_2/n$	$P\bar{1}$	$P\bar{1}$
a, Å	26.7541(6)	14.3716(4)	14.3459(11)
b, Å	26.7541(6)	15.5898(4)	15.5318(13)
c, Å	9.3946(3)	18.3061(5)	18.3357(14)
α, °	90	105.3240(10)	105.271(3)
β, °	90	104.1010(10)	103.906(3)
γ, °	90	100.1840(10)	100.383(3)
V, Å^3	6724.5(4)	3706.73(17)	3694.1(5)
Z	4	2	2
$\rho_{calcd.}$, g·cm^{-3}	1.917	1.891	1.816
μ, mm^{-1}	6.690	7.098	5.655
θ range, °	2.42 – 25.64	2.42 – 30.58	2.32 – 29.56
Miller indices range	$-32 \le h \le 32$ $-32 \le k \le 31$ $-11 \le l \le 11$	$-19 \le h \le 17$ $-20 \le k \le 21$ $-24 \le l \le 24$	$-19 \le h \le 19$ $-19 \le k \le 21$ $-25 \le l \le 25$
Reflections collected/unique	54716/6401	64715/18377	61226/20697
Reflections (I>2σ(I))	5616	16088	14973
R_{int}	0.061	0.037	0.054
GoF	1.161	1.027	1.045
R_1 / wR_2(I> 2σ(I))	R_1 = 0.0369 wR_2 = 0.0660	R_1 = 0.0272 wR_2 = 0.0580	R_1 = 0.0408 wR_2 = 0.0825
R_1 / wR_1 (all data)	R_1 = 0.0473 wR_2 = 0.0691	R_1 = 0.0339 wR_2 = 0.0272	R_1 = 0.0650 wR_2 = 0.0939
$\Delta\rho_{max}/\Delta\rho_{min}$ (e·Å^3)	1.195/-1.120	1.553/-1.415	1.144/-0.971

Table S4. Occupancy of metal atom crystallographic positions in the structures **1**–**9**.

	$[\{Re_{3.35}Mo_{2.65}S_8\}(py)_6]$ (**1**)	$[\{Re_4Mo_2S_8\}(py)_6]$ (**2**)	$[\{Re_3Mo_3S_8\}(py)_6]$ (**3**)
Re^1/Mo^1	0.61/0.39	0.66/0.34	0.52/0.48
Re^2/Mo^2	0.46/0.54	0.63/0.37	0.50/0.50
Re^3/Mo^3	0.59/0.41	0.54/0.46	0.43/0.57
	$[\{Re_{3.30}Mo_{2.70}S_8\}(etpy)_6]$ (**4**)	$[\{Re_4Mo_2S_8\}(etpy)_6]$ (**5**)	$[\{Re_3Mo_3S_8\}(etpy)_6]$ (**6**)
Re^1/Mo^1	0.52/0.48	0.70/0.30	0.47/0.53
Re^2/Mo^2	0.59/0.41	0.76/0.24	0.49/0.51
	$[\{Re_{3.30}Mo_{2.70}S_8\}(tbp)_6]$ (**7**)	$[\{Re_4Mo_2S_8\}(tbp)_6]\cdot(CH_3CN)_2$ (**8**)	$[\{Re_3Mo_3S_8\}(tbp)_6]\cdot(CH_3CN)_2$ (**9**)
Re^1/Mo^1	0.45/0.55	0.68/0.32	0.52/0.48
Re^2/Mo^2	0.60/0.40	0.66/0.34	0.51/0.49
Re^3/Mo^3	0.60/0.40	0.65/0.35	0.49/0.51
Re^4/Mo^4	–	0.66/0.34	0.51/0.49
Re^5/Mo^5	–	0.57/0.43	0.53/0.47
Re^6/Mo^6	–	0.60/0.40	0.48/0.52

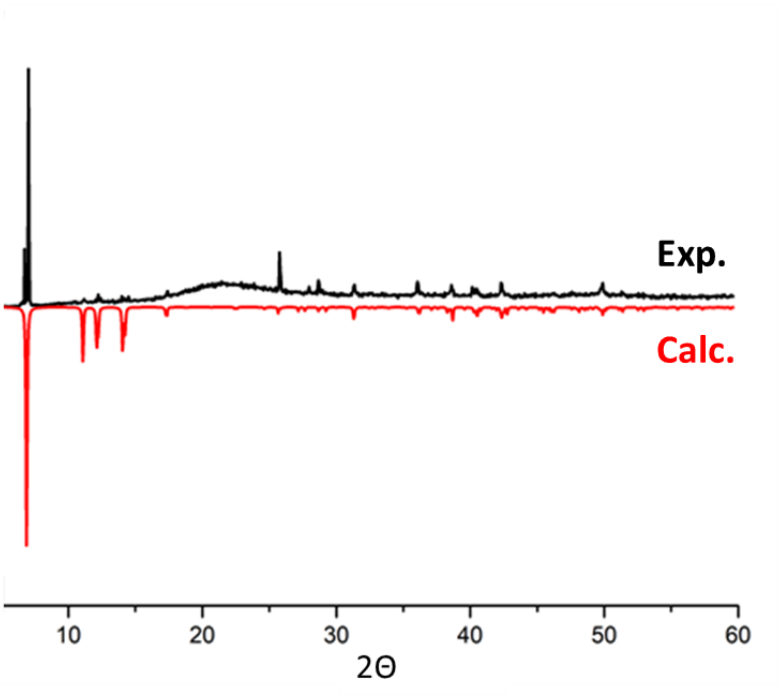

Figure S4. Powder XRD patterns for compound **4**.

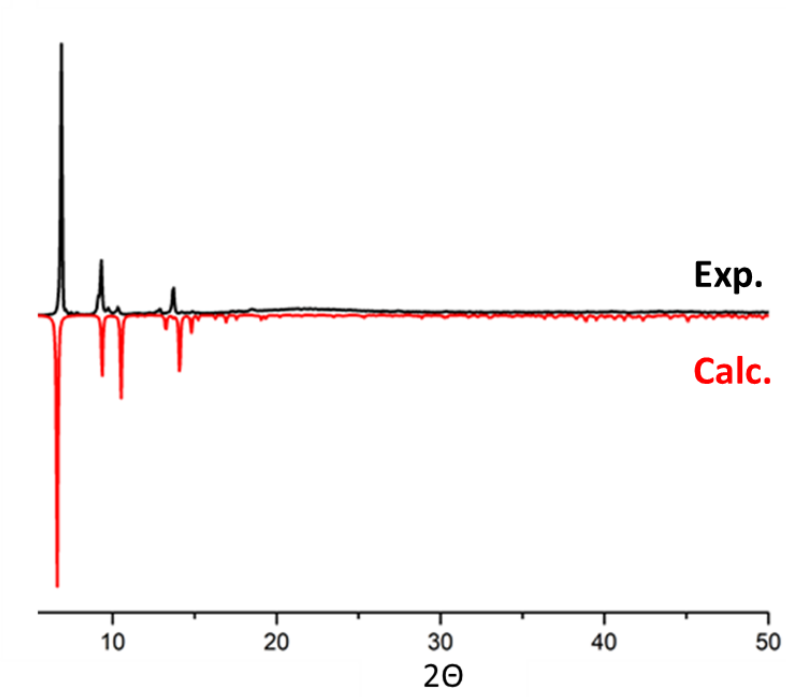

Figure S5. Powder XRD patterns for compound **7**.

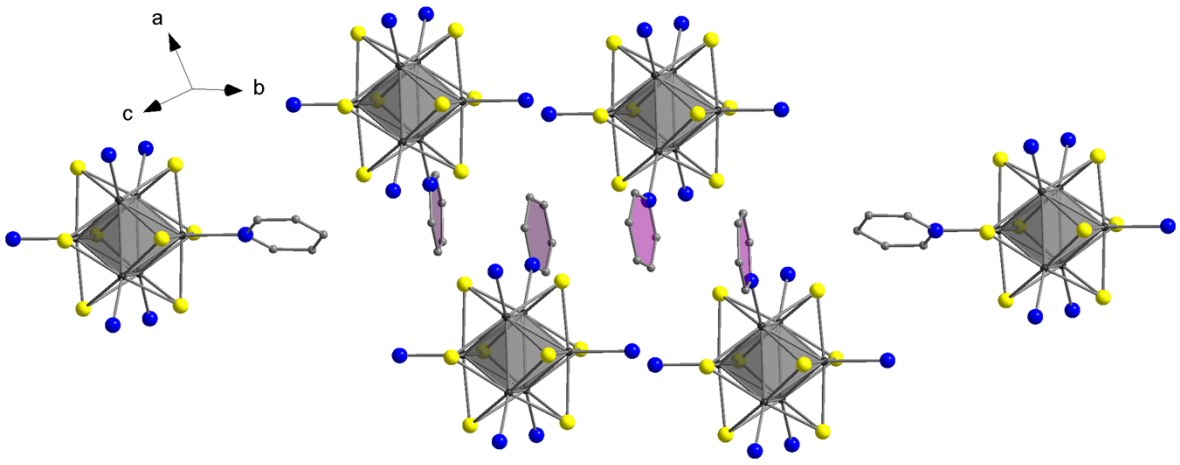

Figure S6. Formation of the isolated tetrameric fragments through the π–π interactions in the structures of compounds **1**–**3**.

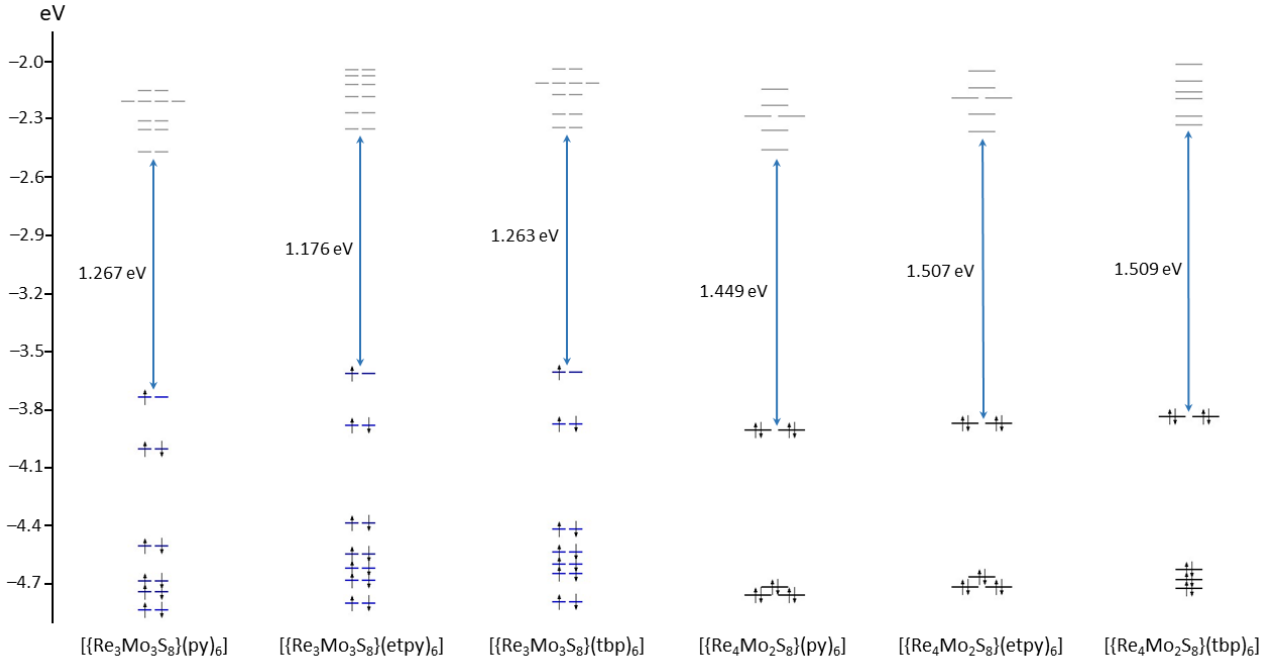

Figure S7. Calculated energy level diagrams and HOMO–LUMO gap values for *mer*-[{$Re_3Mo_3S_8$}L_6] and *trans*-[{$Re_4Mo_2S_8$}L_6] clusters (L = py, etpy, tbp)