

# From $K_6[Re_{6-x}Mo_xS_8(CN)_5]$ Solid Solution to Individual Cluster Complexes: Separation and Investigation of $[Re_4Mo_2S_8(CN)_6]^{n-}$ and $[Re_3Mo_3S_8(CN)_6]^{n-}$ Heterometallic Clusters

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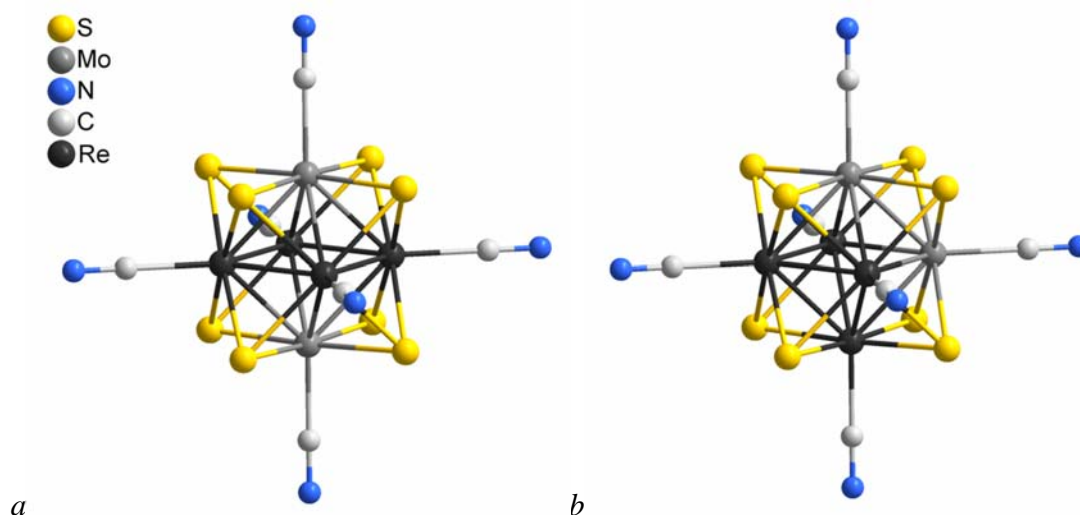
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## EXAFS measurements and data fitting

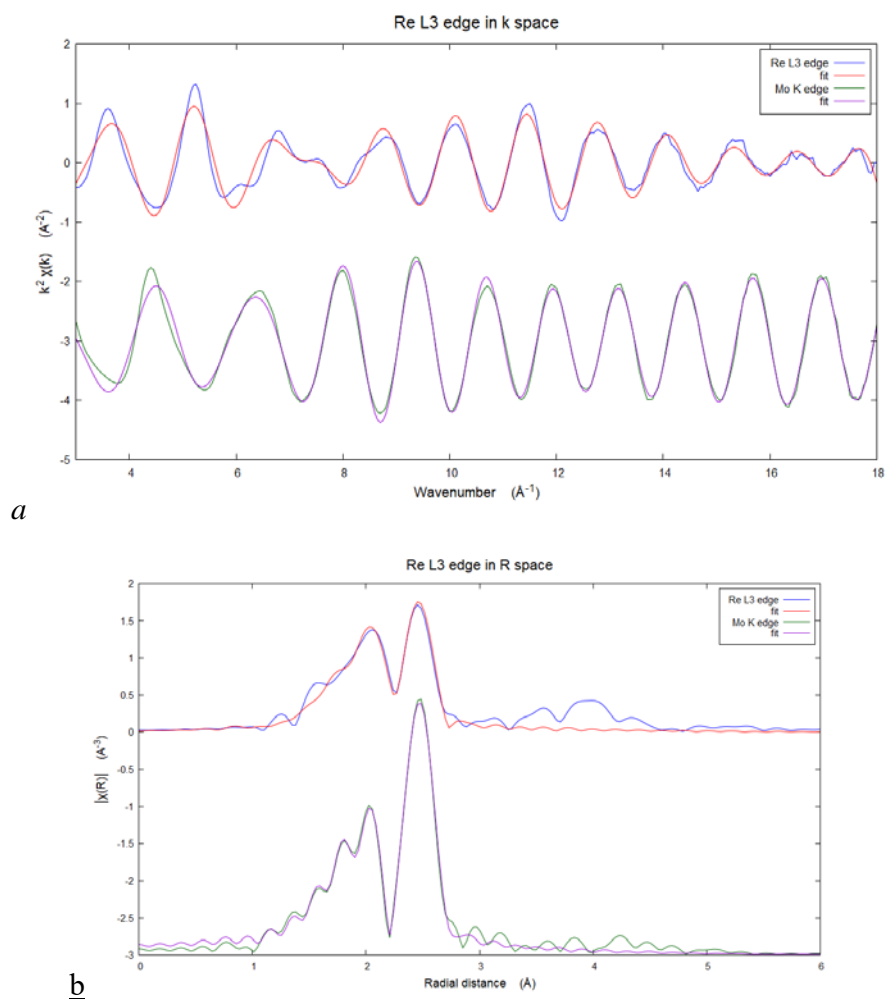
Both data for Re-L3 edge and Mo K-edge has been fitted using a single E0 for each edge, and constrain the Mo–C and Re–C path to have the same Debye-Waller factor. The others constrain are induced by identity the Mo–Re distance is the same of Re–Mo.



**Figure S1.** Cluster core isomerism in  $[\text{Re}_4\text{Mo}_2\text{S}_8(\text{CN})_6]$ : a) *trans*- $[\text{Re}_4\text{Mo}_2\text{S}_8(\text{CN})_6]$  b) *cis*- $[\text{Re}_4\text{Mo}_2\text{S}_8(\text{CN})_6]$  models used for data fitting

**Table S1.** Final fitting parameters of EXAFS spectra of  $(\text{Bu}_4\text{N})_4[\text{Re}_4\text{Mo}_2\text{S}_8(\text{CN})_6]$  (**4**) with *trans*- $[\text{Re}_4\text{Mo}_2\text{S}_8(\text{CN})_6]$  model.

Mo K edge : k-range=3-19 R-range= 1–3 weight = 1,2,3 R-factor $k^2=0.00760$ $S_0^2 = 1.01(7)$				
	N	R	$\sigma^2$	e0
C	1	2.18(3)	0.0005(2)	4.2(1.1)
S	4	2.420(7)	0.0024(1)	4.2(1.1)
Re	4	2.644(3)	0.0024(2)	4.2(1.1)
Re L <sub>3</sub> edge : k-range=2.9-17.8 R-range= 1.2–3 weight = 1,2,3 R-factor $k^2=0.02355$ $S_0^2 = 0.90(7)$				
	N	R	$\sigma^2$	e0
C	1	2.13(2)	0.0005(2)	6.8(8)
S	4	2.413(5)	0.00254(6)	6.8(8)
Mo	2	2.644(3)	0.0021(2)	6.8(8)
Re	2	2.592(4)	0.0021(3)	6.8(8)

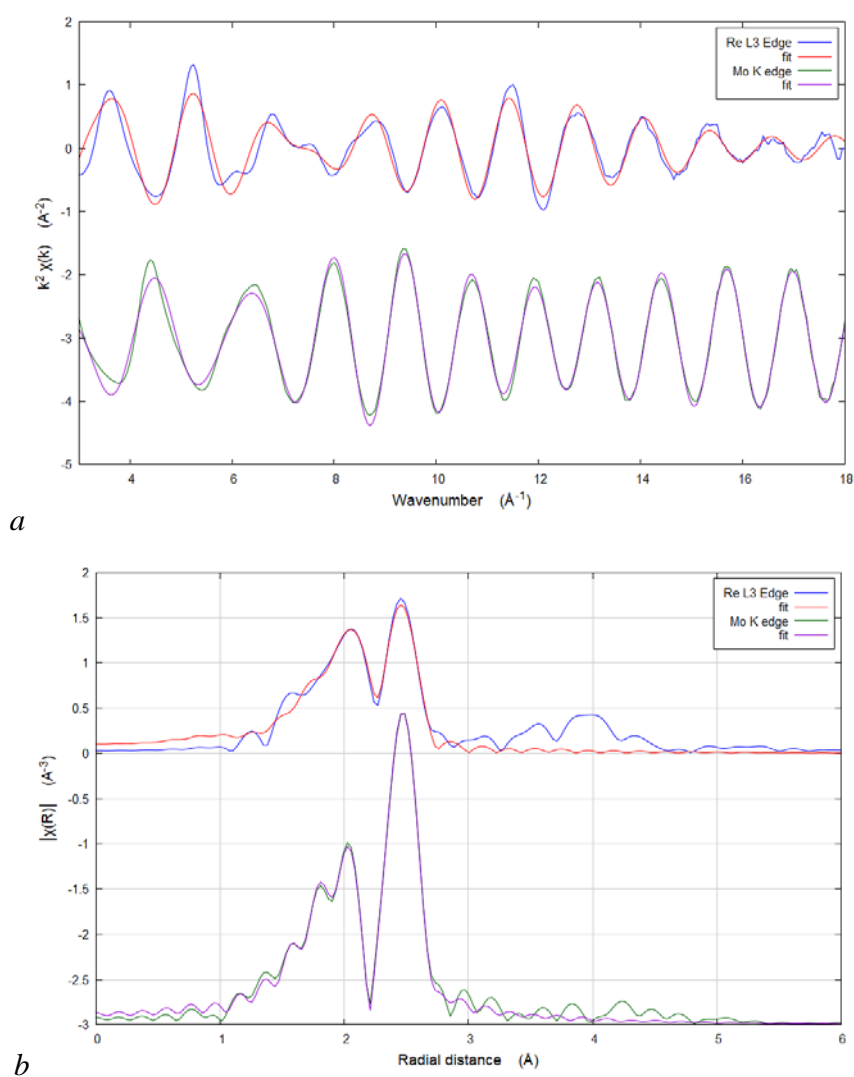


**Figure S2.** a) EXAFS measurements for  $(\text{Bu}_4\text{N})_4[\text{Re}_4\text{Mo}_2\text{S}_8(\text{CN})_6]$  (**4**) (weighted by  $k^2$ ), b) Fourier transform magnitudes. Re L3-edge experimental curves (blue), model fit with *trans*- $[\text{Re}_4\text{Mo}_2\text{S}_8(\text{CN})_6]$  (red); Mo K-edge experimental curve (green), model fit with *trans*- $[\text{Re}_4\text{Mo}_2\text{S}_8(\text{CN})_6]$  (purple).

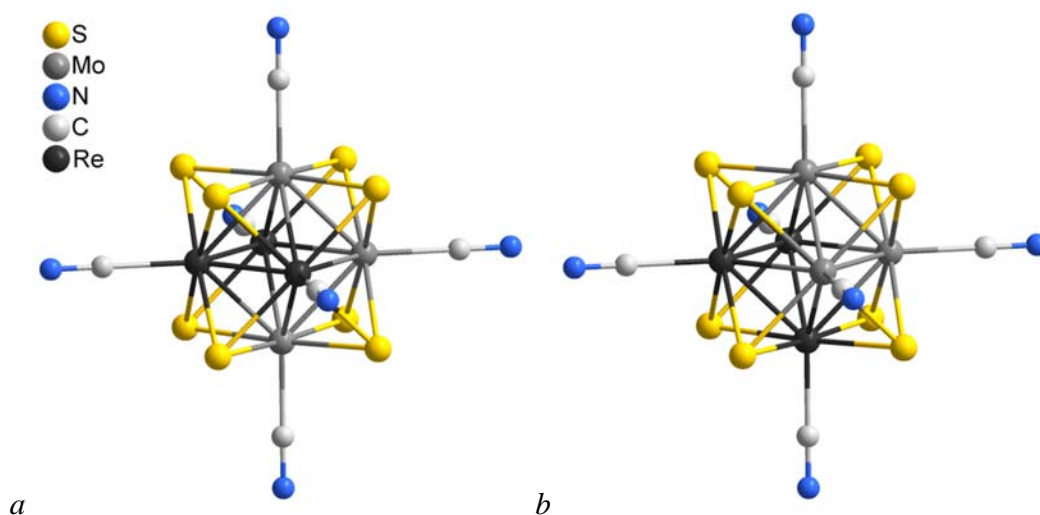
**Table S2.** Final fitting parameters of EXAFS spectra of  $(\text{Bu}_4\text{N})_4[\text{Re}_4\text{Mo}_2\text{S}_8(\text{CN})_6]$  (**4**) with *cis*- $[\text{Re}_4\text{Mo}_2\text{S}_8(\text{CN})_6]$  model.

Mo K edge : k-range=3-19 R-range= 1–3 weight = 1,2,3 R-factor $k^2=0.00531$ $S_0^2 = 094(7)$				
	N	R	$\sigma^2$	$\epsilon_0$
C	1	2.13(3)	0.001(2)	4.6(1.0)
S	4	2.419(5)	0.0026(5)	4.6(1.0)
Re	3	2.644(3)	0.0017(2)	4.6(1.0)
Mo	1	2.80(3)	0.005(3)	4.6(1.0)

Re L <sub>3</sub> edge : k-range=2.9-17.8 R-range= 1.2-3 weight = 1,2,3 R-factor k <sup>2</sup> =0.02759 S <sub>0</sub> <sup>2</sup> = 0.90(7)				
	N	R	σ <sup>2</sup>	e <sub>0</sub>
C	1	2.20(5)	0.001(2)	8.8(8)
S	4	2.413(5)	0.00254(6)	8.8(8)
Mo	2	2.644(3)	0.0017(2)	8.8(8)
Re	2	2.593(4)	0.0027(4)	8.8(8)



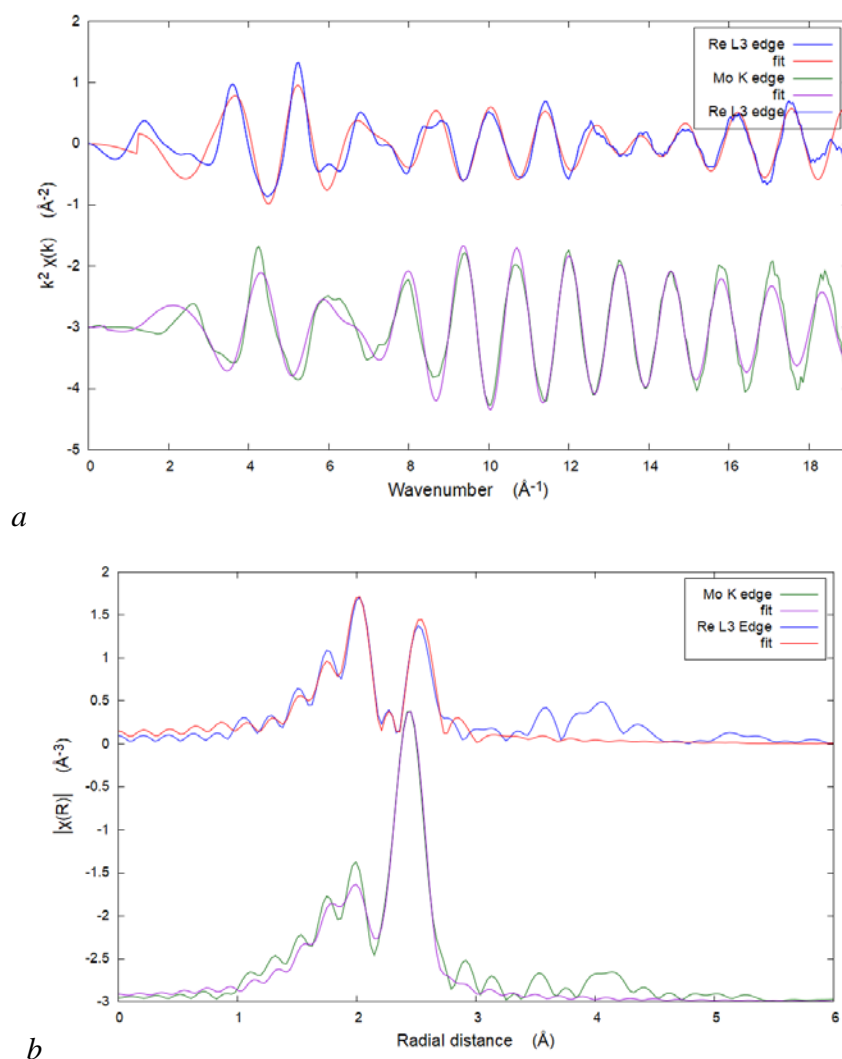
**Figure S3.** a) EXAFS measurements for (Bu<sub>4</sub>N)<sub>4</sub>[Re<sub>4</sub>Mo<sub>2</sub>S<sub>8</sub>(CN)<sub>6</sub>] (**4**) (weighted by k<sup>2</sup>), b) Fourier transform magnitudes. Re L<sub>3</sub>-edge experimental curves (blue), model fit with *cis*-[Re<sub>4</sub>Mo<sub>2</sub>S<sub>8</sub>(CN)<sub>6</sub>] (red); Mo K-edge experimental curve (green), model fit with *cis*-[Re<sub>4</sub>Mo<sub>2</sub>S<sub>8</sub>(CN)<sub>6</sub>] (purple).



**Figure S4.** Cluster core isomerism in  $[\text{Re}_3\text{Mo}_3\text{S}_8(\text{CN})_6]$ : a) *mer*- $[\text{Re}_3\text{Mo}_3\text{S}_8(\text{CN})_6]$  b) *fac*- $[\text{Re}_3\text{Mo}_3\text{S}_8(\text{CN})_6]$  models used for data fitting.

**Table S3.** Final fitting parameters of the EXAFS spectra of  $\text{K}_5[\text{Re}_3\text{Mo}_3\text{S}_8(\text{CN})_6]$  (**5**) with *fac*- $[\text{Re}_3\text{Mo}_3\text{S}_8(\text{CN})_6]$  model.

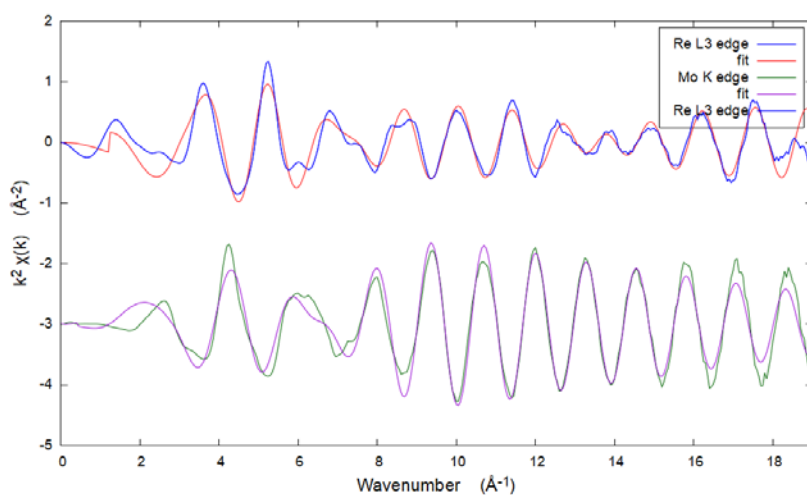
Mo K edge : k-range=3-19 R-range= 1–3 weight = 1,2,3 R-factor $k^2=0.00760$ $S_0^2 = 0.91 (1)$				
	N	R	$\sigma^2$	$e_0$
C	1	2.17(7)	0.00100	0.8(9)
S	4	2.45(1)	0.0036(1)	0.8(9)
Mo	2	2.75(2)	0.0026(8)	0.8(9)
Re	2	2.630(6)	0.0020(5)	0.8(9)
Re L <sub>3</sub> edge : k-range=2.9-17.8 R-range= 1.2–3 weight = 1,2,3 R-factor $k^2=0.02355$ $S_0^2 = 0.88(6)$				
	N	R	$\sigma^2$	$e_0$
C	1	2.11(3)	0.00100	5.8(9)
S	4	2.407(6)	0.0023(5)	5.8(9)
Mo	2	2.630(6)	0.0020(5)	5.8(9)
Re	2	2.608(4)	0.0015(5)	5.8(9)



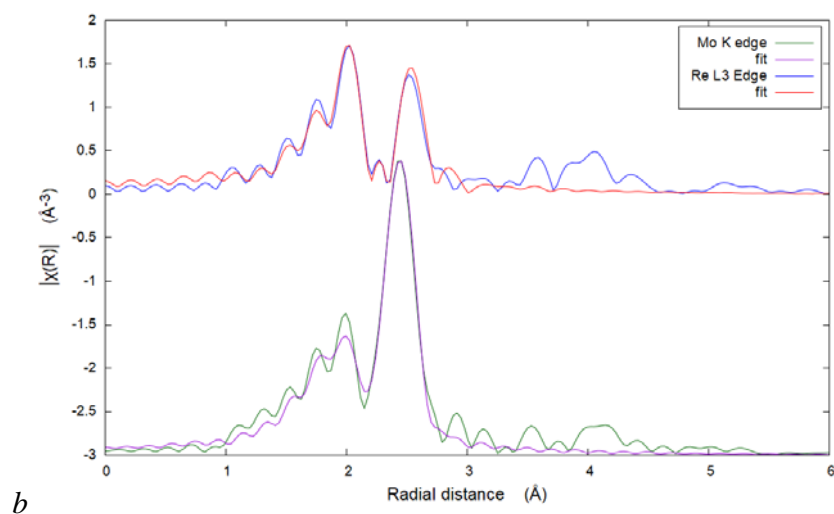
**Figure S5.** a) EXAFS measurements for  $K_5[Re_3Mo_3S_8(CN)_6]$  (**5**) (weighted by  $k^2$ ), b) Fourier transform magnitudes. Re L3-edge experimental curves (blue), model fit with *fac*- $[Re_3Mo_3S_8(CN)_6]$  (red); Mo K-edge experimental curve (green), model fit with *fac*- $[Re_3Mo_3S_8(CN)_6]$  (purple).

**Table S4.** Final fitting parameters of the EXAFS spectra of  $\text{K}_5[\text{Re}_3\text{Mo}_3\text{S}_8(\text{CN})_6]$  (**5**) with *mer*- $[\text{Re}_3\text{Mo}_3\text{S}_8(\text{CN})_6]$  model.

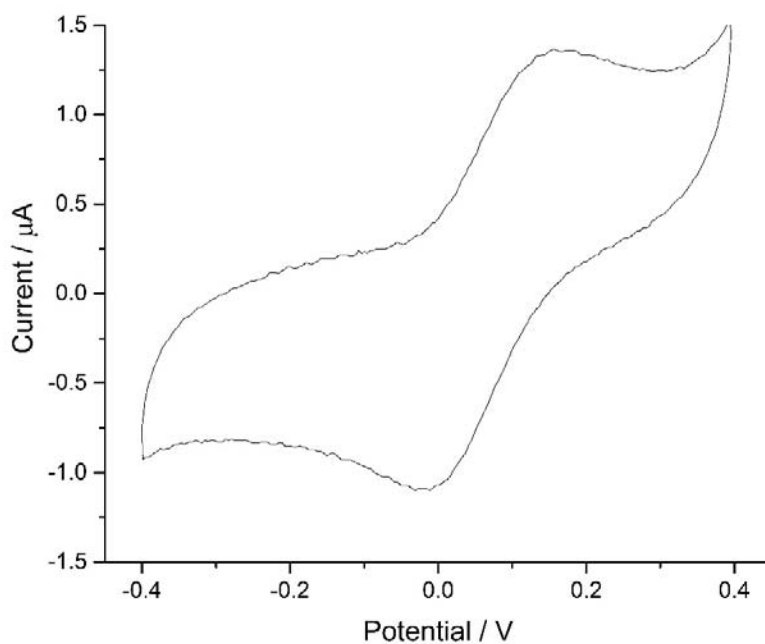
Mo K edge : k-range=3-19 R-range= 1–3 weight = 1,2,3 R-factor $k^2=0.00760$ $S_0^2 = 1.33$ (1)				
	N	R	$\sigma^2$	$e_0$
C	1	2.13(5)	0.001	0.08(9)
S	4	2.457(8)	0.0062(5)	0.08(9)
Re	2.667	2.642(5)	0.0042(7)	0.08(9)
Mo	1.333	2.741(3)	0.0010(8)	0.08(9)
Re L <sub>3</sub> edge : k-range=2.9-17.8 R-range= 1.2–3 weight = 1,2,3 R-factor $k^2=0.02355$ $S_0^2 = 0.88$ (6)				
	N	R	$\sigma^2$	$e_0$
C	1	2.12(3)	0.001	6.8(9)
S	4	2.41(1)	0.0021(6)	6.8(9)
Mo	2.667	2.642(5)	0.0042(5)	6.8(9)
Re	1.333	2.612(6)	0.0010(7)	6.8(9)



*a*



**Figure S6.** a) EXAFS measurements for  $\text{K}_5[\text{Re}_3\text{Mo}_3\text{S}_8(\text{CN})_6]$  (**5**) (weighted by  $k^2$ ), b) Fourier transform magnitudes. Re L3-edge experimental curves (blue), model fit with *mer*- $[\text{Re}_3\text{Mo}_3\text{S}_8(\text{CN})_6]$  (red); Mo K-edge experimental curve (green), model fit with *mer*- $[\text{Re}_3\text{Mo}_3\text{S}_8(\text{CN})_6]$  (purple).



**Figure S7.** Cyclic voltammetry curve for the  $\text{K}_5[\text{Re}_4\text{Mo}_2\text{S}_8(\text{CN})_6]$  salt in aqueous solution vs Ag/AgCl reference electrode. Scan rate was  $50 \text{ mV} \cdot \text{s}^{-1}$ .