Electronic Supplementary Information

Pressure-dependent luminescence spectroscopy of molybdenum(IV) oxo complexes

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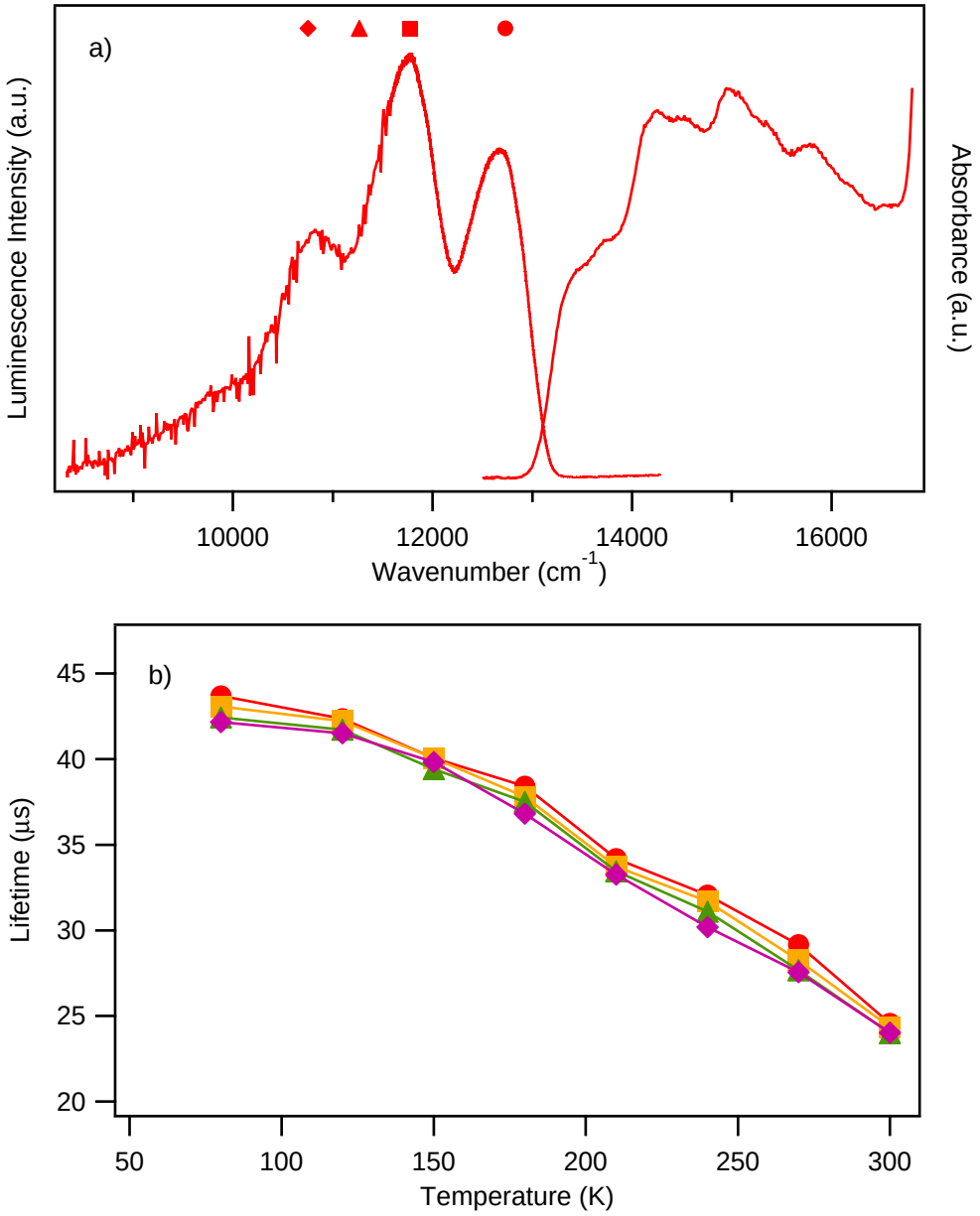


Figure S1. (a) Corrected luminescence spectrum (left) and absorption (right) spectra of [MoOCl(CN-*t*-Bu)$_4$]BPh$_4$ at 15K. (b) Temperature-dependent luminescence lifetimes of [MoOCl(CN-*t*-Bu)$_4$]BPh$_4$ at 10750, 11270, 11780 and 12730 cm^{-1}.

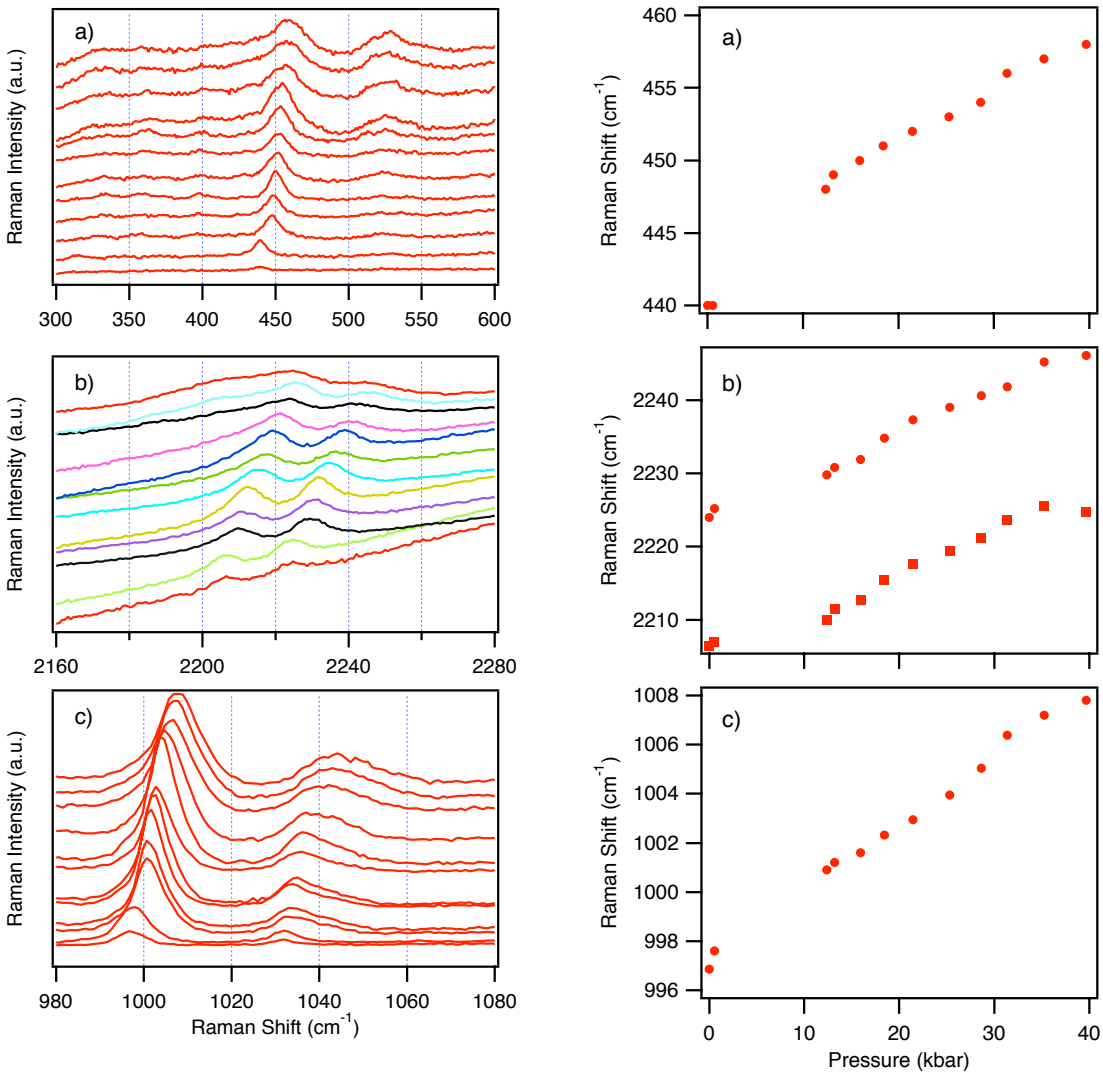


Figure S2. Pressure-dependent Raman spectra (left) and band maxima (right) of [MoOCl(CN-*t*-Bu)$_4$]BPh$_4$ of vibrational modes (a) Mo-C, (b) C-N and (c) BPh$_4$ at (from bottom to top) 1 bar, 1, 12, 13, 16, 18, 21, 25, 29, 31, 35 and 40 kbar.

Slopes (cm^{-1}/kbar) (for pressures higher than 10 kbar):

(a) 0.36 ± 0.05

(b) low frequency mode : 0.53 ± 0.05 and high frequency mode : 0.58 ± 0.05

(c) 0.28 ± 0.05

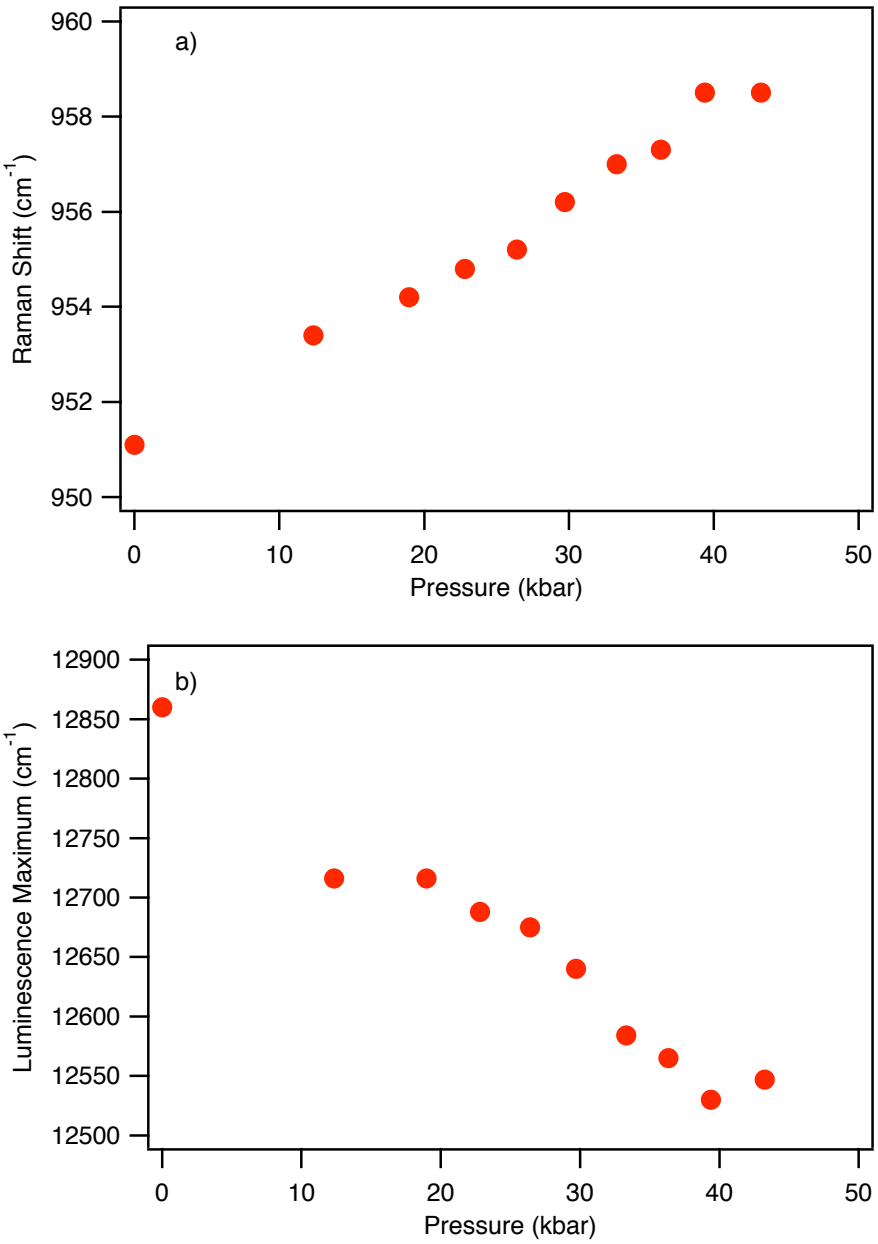


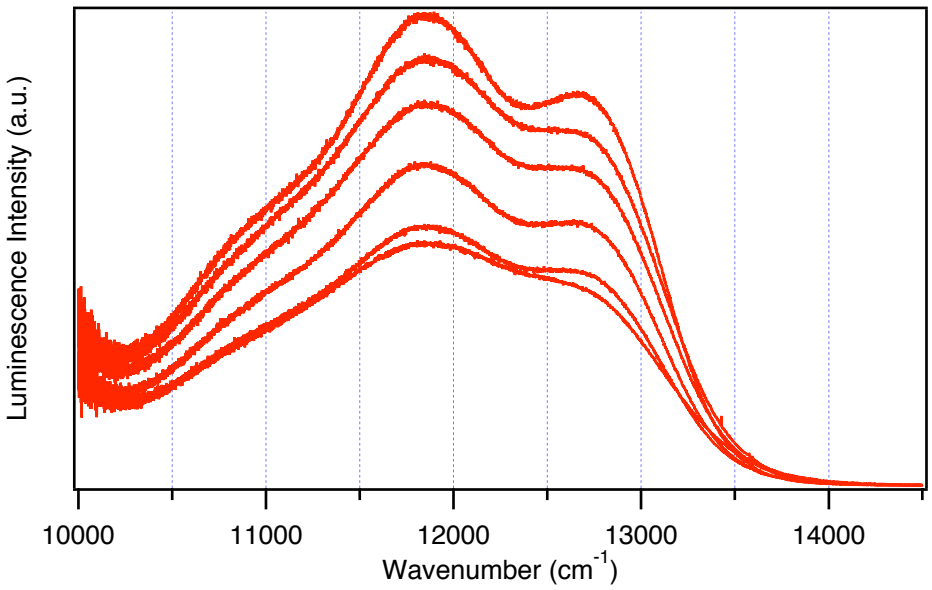
Figure S3. (a) Raman maxima for the Mo-oxo stretching mode of $[MoOF(py)_4]BPh_4$ as a function of pressure. (b) Luminescence maxima of $[MoOF(py)_4]BPh_4$ as a function of pressure.

Slopes (cm^{-1}/kbar)

(a) 0.18 ± 0.05

(b) -7.5 ± 0.5

a)



b)

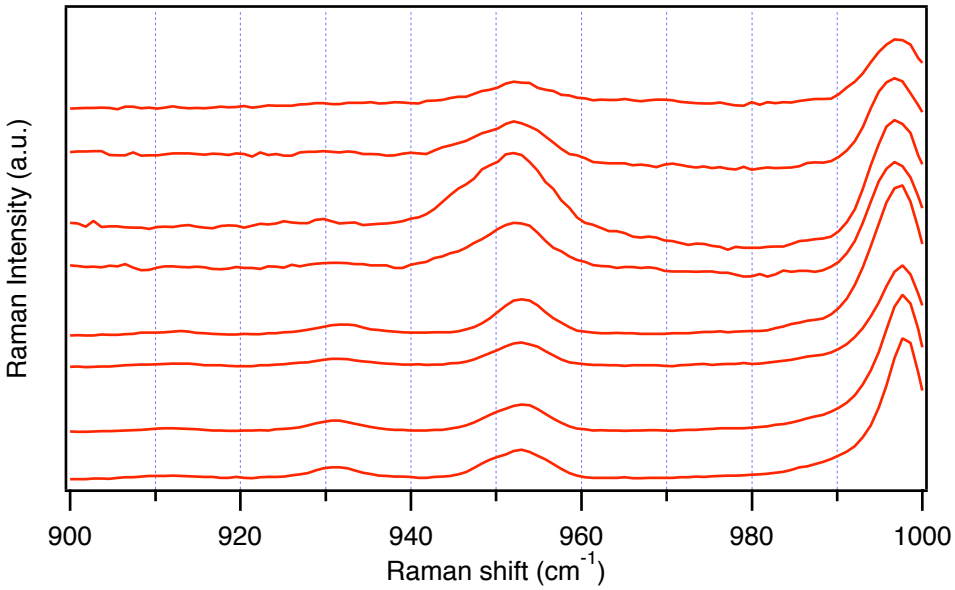
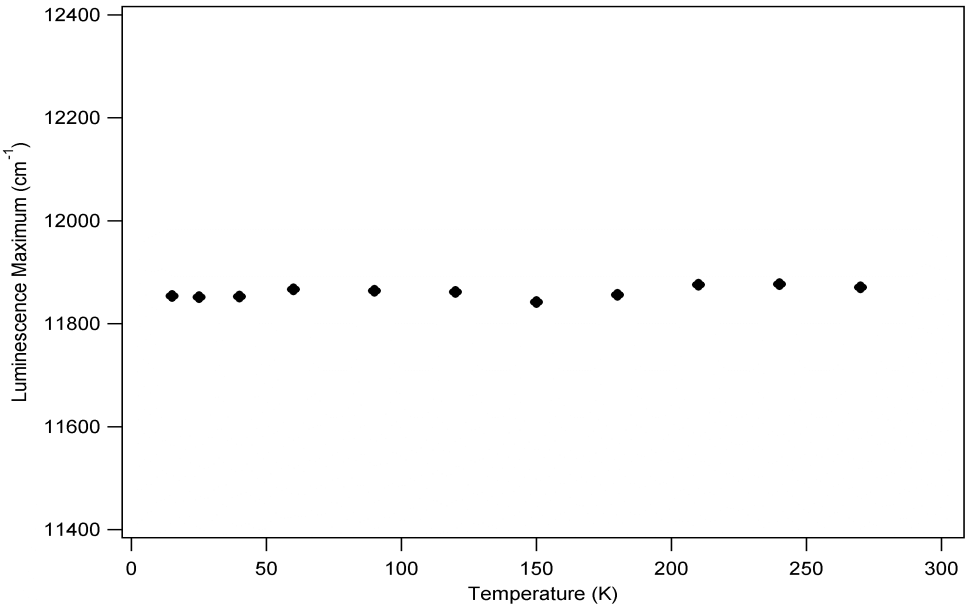


Figure S4. (a) Temperature-dependent luminescence spectra of [MoOCl(CN-*t*-Bu)$_4$]BPh$_4$ at (from top to bottom) 15, 60, 120, 150, 180, 270 K and (b) Temperature-dependent Raman spectra of [MoOCl(CN-*t*-Bu)$_4$]BPh$_4$ at (from top to bottom) 15, 60, 120, 150, 180, 210, 240, 270 K.

a)



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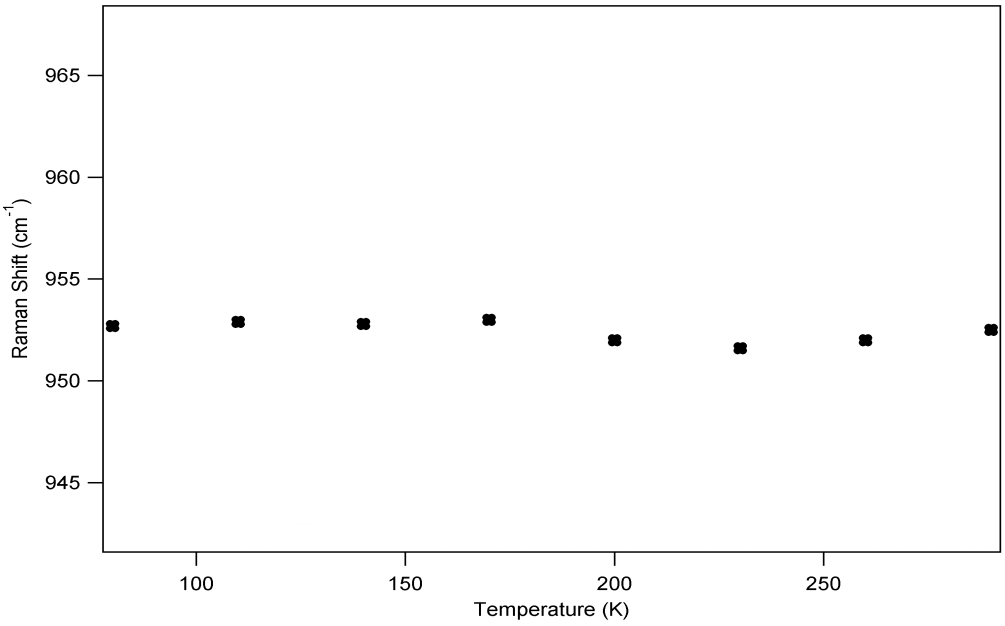


Figure S5. (a) Temperature-dependent luminescence band maxima of $[MoOCl(CN\text{-}t\text{-}Bu)_4]BPh_4$ at (from top to bottom) 15, 60, 120, 150, 180, 270 K and (b) Temperature-dependent Mo-O Raman band maxima of $[MoOCl(CN\text{-}t\text{-}Bu)_4]BPh_4$ at (from top to bottom) 15, 60, 120, 150, 180, 210, 240, 270 K.

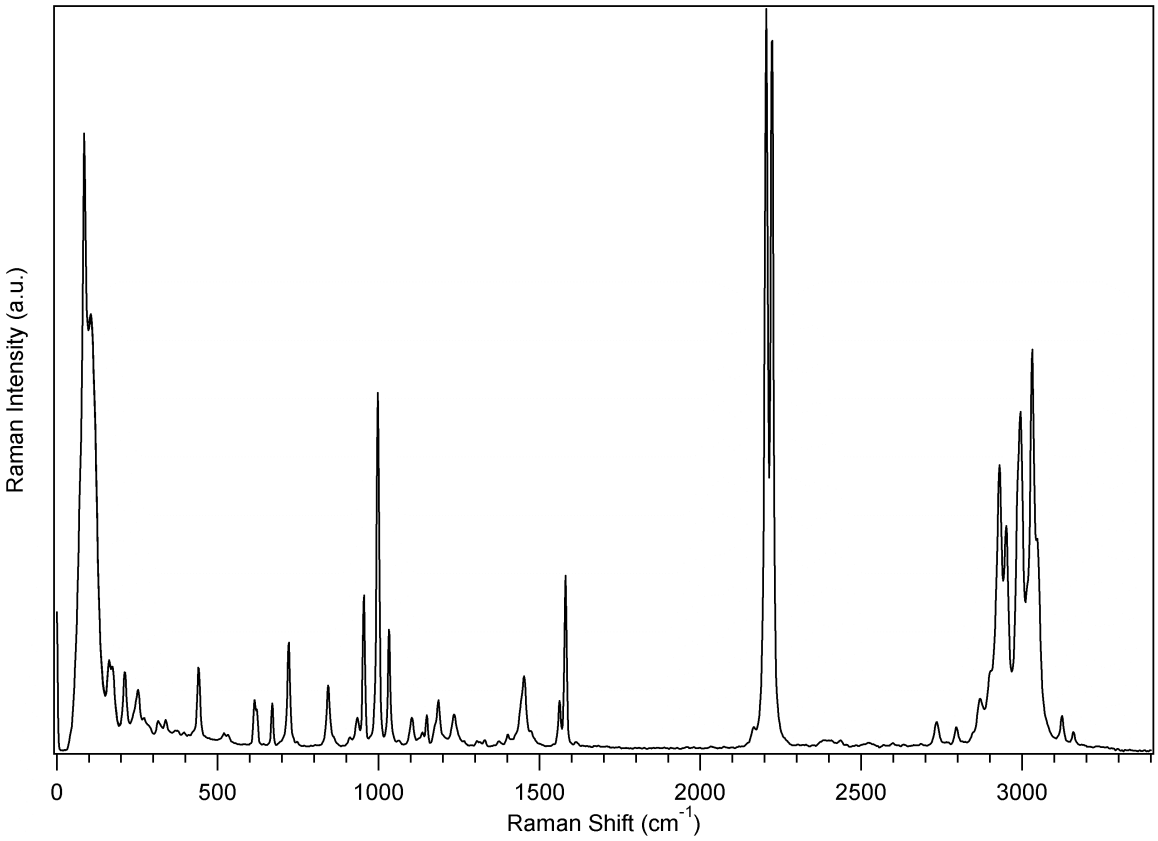
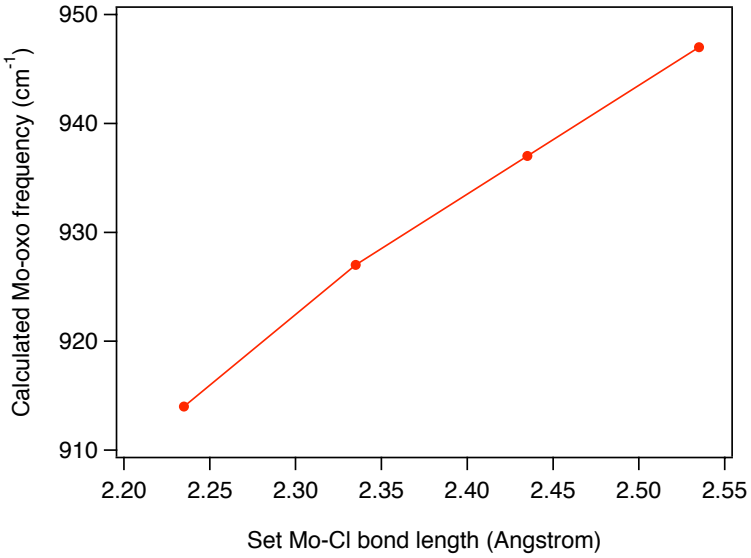


Figure S6. Off-resonance Raman spectrum of $[MoOCl(CN\text{-}t\text{-}Bu)_4]BPh_4$ using 1034 nm excitation.

a)



b)

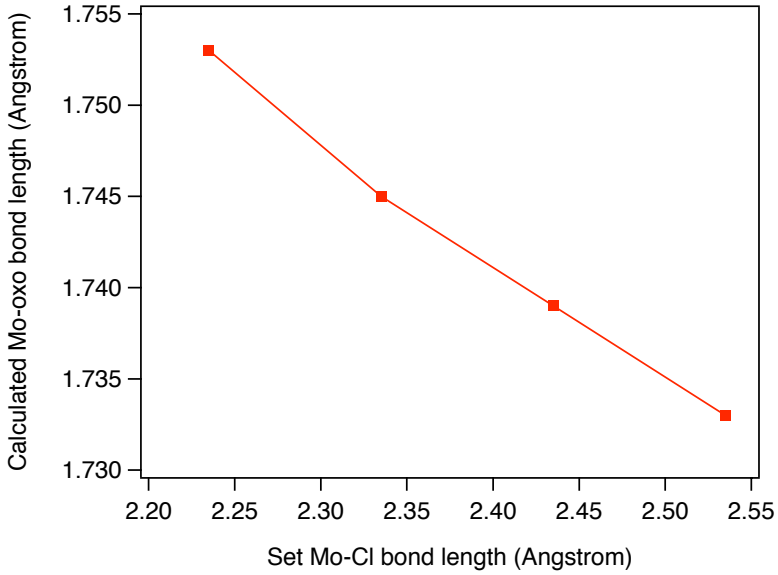


Figure S7. (a) Calculated Mo-oxo stretching frequencies of $[MoOCl(CN\text{-}t\text{-}Bu)_4]^+$ as a function of Mo-Cl bond length. (b) Calculated Mo-oxo bond length as a function of Mo-Cl bond length in $[MoOCl(CN\text{-}t\text{-}Bu)_4]^+$. DFT calculations were carried out as described in the text. The rightmost point along the Mo-Cl bond length axis corresponds to the optimized structure without imposing a specific Mo-Cl bond length.