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Supporting Information

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"Push-Pull" Molybdenum Trisdithiolenes Allow for Rapid Nonconventional Binding of Ethylene at Ligand Sulfur Atoms

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General. Experiments were conducted under inert (N_2 or Ar) atmosphere using standard dry-box (M Braun UniLab) or Schlenk-type techniques except where noted. Compounds $Mo(tfd)_3$,[1] $Mo(bdt)_3$,[2] $[NEt_4]_2[MoO(tfd)_2]$,[3] $Mo(bdt)_2(PPh_2Me)_2$,[4] $S_2C_2(CF_3)_2$[5] and $Na_2S_2C_2(CN)_2$[6] were prepared by literature procedures. All other chemicals were purchased from Sigma Aldrich or Alpha Aesar and used as received. Dichloromethane, hexanes and tetrahydrofuran (THF) were dried/deoxygenated using an M Braun solvent purification system (MB-SPS). Acetonitrile-d_3 (CD_3CN), chloroform-d ($CDCl_3$) and dichloromethane-d_2 (CD_2Cl_2) were dried/degassed over CaH_2 and vacuum-transferred prior to use. Acetone-d_6 and chloroform were dried over activated molecular sieves and deoxygenated (with argon or N_2 purge) prior to use. Ethanol was dried/degassed over magnesium metal (with trace I_2) and vacuum-transferred before using. Silica gel (60-230 mesh) was used as received or dried/deoxygenated under vacuum (>3h, 80°C), where noted. UV-vis spectra were obtained on a Cary 14 spectrophotometer. ^1H NMR spectra were obtained on Varian Gemini 200 MHz or Unity/Inova Varian 500 MHz spectrometers. Residual proton peaks were used as reference: ^1H (δ, ppm, acetone-d_6, 2.05; acetonitrile-d_3, 1.94; chloroform-d, 7.26; dichloromethane-d_2, 5.32). ^{19}F NMR data were recorded on a Unity/Inova Varian 500 MHz spectrometer at 470 MHz and referenced to external trifluoroacetic acid (δ, ppm, -76.55). In some NMR experiments, 3,5-bis(trifluoromethyl)bromobenzene ("BTBB") was used as an internal standard ($^1H/^{19}F$). Elemental analyses were conducted at Guelph (Chemisar) Laboratories, Guelph, ON, Canada.

Reaction of $Mo(tfd)_3$ with excess ethylene (low concentration; monitored by UV-vis). $Mo(tfd)_3$ (5.9 mg, 0.0076 mmol) was placed in a flask with 45.0 mL of CH_2Cl_2 and a stir bar. The flask was sealed and the mixture was stirred at RT for 20 min to completely dissolve the $Mo(tfd)_3$, affording a violet colored solution (0.17 mM in $Mo(tfd)_3$). From the resulting solution, 4.0 mL was taken and placed in a sealable quartz cuvette (1.0 cm pathlength). Ethylene was introduced to the sample by allowing the gas to gently bubble through the solution for approximately 2 min to give a saturated solution. The cuvette was sealed under ethylene. UV-vis spectra (scan range: 250-850 nm) were collected over time after ethylene addition ($T \approx 25°C$) (see below, Figure S1):

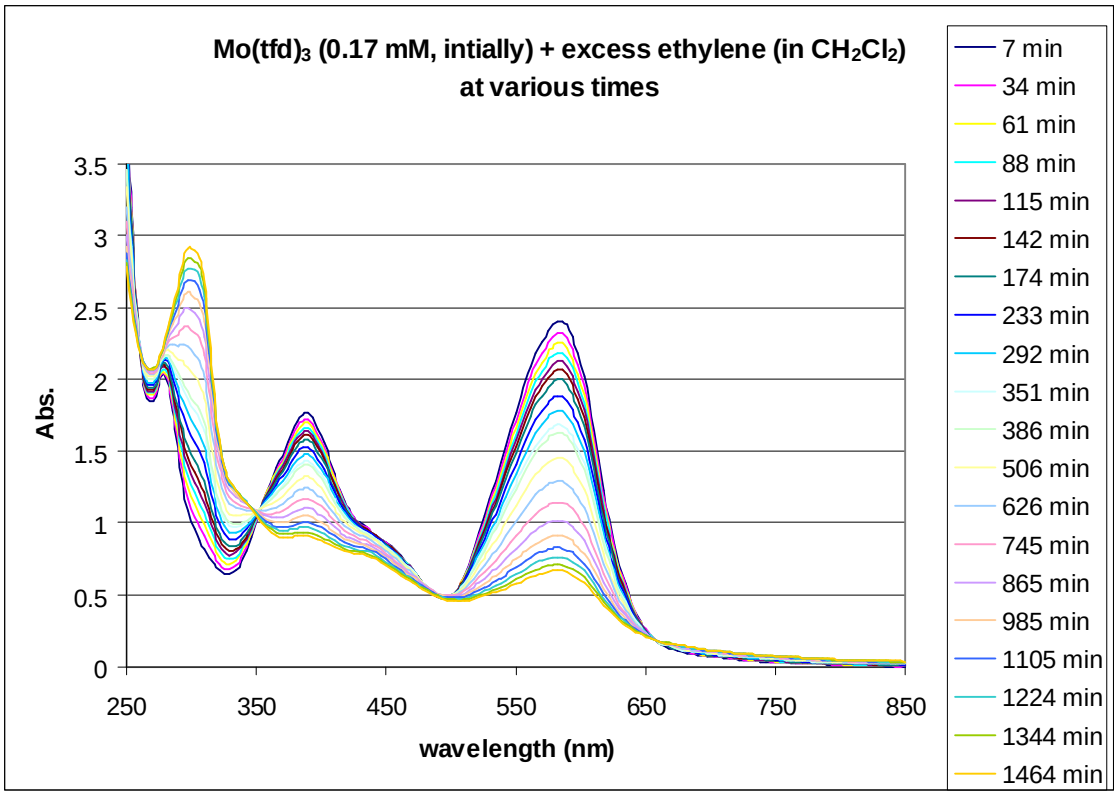

Figure S1. UV-vis spectra (solvent = CH_2Cl_2) monitoring the reaction of $Mo(tfd)_3$ (0.17 mM initially) with excess ethylene (saturated CH_2Cl_2 solution) ($T \approx 25^oC$).

Comments: The consumption of $Mo(tfd)_3$ was monitored by decay of its characteristic absorption bands (λ_{max} = 390 nm, λ_{max} = 582 nm). A new peak grows in at λ_{max} = 298 nm. The half-life ($t_{1/2}$) for this reaction is approximately 11 h; after >20 h, the consumption of $Mo(tfd)_3$ was not complete. Under the same conditions, $Mo(tfd)_2(bdt)$ is completely consumed in the presence of ethylene in <2 min (see below).

Reaction of $Mo(tfd)_3$ with excess ethylene (monitored by ^1H NMR). $Mo(tfd)_3$ (9.4 mg, 0.012 mmol) was weighed into a J. Young NMR tube. CD_2Cl_2 (0.6 mL) was added, which partially dissolved the dark colored solid, giving a faintly violet colored solution. Ethylene was added by allowing the gas to bubble through the solution for approximately 3 min and the tube was sealed under ethylene. The mixture was protected from light and left to react at RT for 48 h. A ^1H NMR spectrum was collected. The spectrum shows only unreacted ethylene and 5,6-dihydro-2,4-bis(trifluoromethyl)-1,4-dithiin. ^1H NMR (200 MHz, CD_2Cl_2) δ 3.30 (s, dihydrodithiin $C\underline{H}_2C\underline{H}_2$), 5.40 (s, unreacted ethylene).

Reaction of $Mo(bdt)_3$ with excess ethylene (low concentration; monitored by UV-vis). $Mo(bdt)_3$ (10.5 mg, 0.0203 mmol) was placed in a flask with 25.0 mL of CH_2Cl_2 and a stir bar. The flask was sealed and the mixture was stirred, at RT, for 15 min to dissolve the $Mo(bdt)_3$, to afford a green solution with 0.812 mM in $Mo(bdt)_3$. Using a 1 mL syringe, 0.78 mL ($6.3x10^{-4}$ mmol of $Mo(bdt)_3$) of this green solution was placed in a

graduated cylinder and diluted to 4.0 mL. This faintly green solution (0.16 mM in $Mo(bdt)_3$) was placed in a sealable quartz cuvette (1.0 cm pathlength). Ethylene was added by allowing the gas to gently bubble through the green solution for approximately 2 min to give a saturated solution. The cuvette was sealed under ethylene and UV-vis data were collected over time (scan range: 250 nm – 850 nm) (T ≈ 25°C). See spectra below (Figure S2):

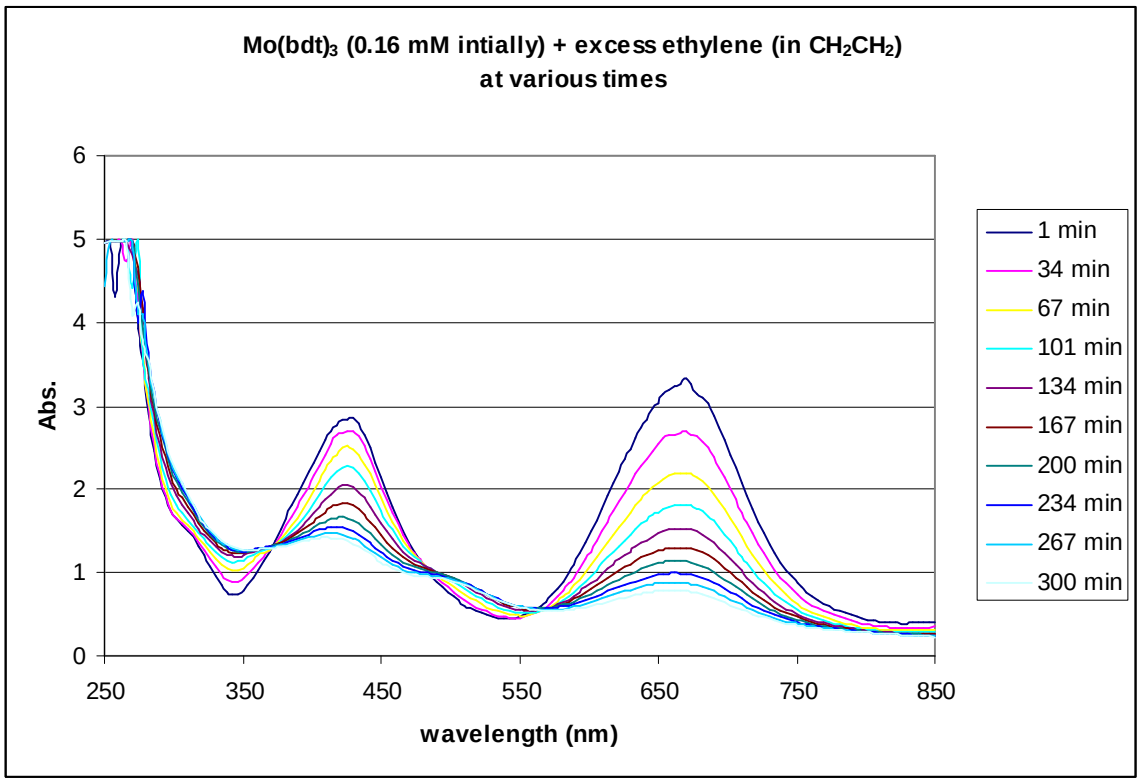

Figure S2. UV-vis spectra (solvent = CH_2Cl_2) monitoring the reaction of $Mo(bdt)_3$ (0.16 mM initially) with excess ethylene (saturated CH_2Cl_2 solution) (T ≈ 25°C).

Comments: The consumption of $Mo(bdt)_3$ was followed by decay of its characteristic absorbance signals (λ_{max} = 430 nm and 670 nm). As seen in Fig. S2 (c.f., Fig. S1), this reaction is considerably faster ($t_{1/2}$ ≈ 2 h) than the reaction of $Mo(tfd)_3$ with ethylene under the same conditions ($t_{1/2}$ ≈ 11 h). However, it is much slower than the reactions of the mixed-ligand complexes ($Mo(tfd)_2(bdt)$ or $Mo(bdt)_2(tfd)$) with ethylene (see below).

Reaction of $Mo(bdt)_3$ with excess ethylene (monitored by ^1H NMR). $Mo(bdt)_3$ (7.0 mg, 0.014 mmol) was weighed into a J. Young NMR tube. CD_2Cl_2 (0.6 mL) was added, which partially dissolved the dark colored solid, giving a green colored solution. Ethylene was added by allowing the gas to bubble through the solution for approximately 3 min and the tube was sealed under ethylene. The mixture was protected from light and left to reaction at RT for 48 h. A ^1H NMR spectrum was collected. The spectrum shows unreacted $Mo(bdt)_3$ and ethylene, as well as 2,3-dihydro-1,4-benzodithiin and metal decomposition products ($(Mo(bdt)_2)_x$). ^1H NMR (200 MHz, CD_2Cl_2) δ 3.26 (s,

dihydrodithiin $C\underline{H}_2C\underline{H}_2$), 5.40 (s, unreacted ethylene), 6.18-7.70 (ov m, $((Mo(bdt)_2)_x)$), 7.00 (m, dihydrodithiin $S_2(C_6\underline{H}_4)$), 7.14 (m, dihydrodithiin $S_2(C_6\underline{H}_4)$), 7.43 (m, unreacted $Mo(bdt)_3$), 8.19 (m, unreacted $Mo(bdt)_3$).

Reaction of $Mo(tfd)_2(bdt)$ with excess ethylene (low concentration; monitored by UV-vis). $Mo(tfd)_2(bdt)$ (10.3 mg, 0.0150 mmol) was weighed into a vial and dissolved in 2.0 mL of CH_2Cl_2, giving a solution with 0.00748 M in dithiolene. From this green-blue solution, 87 µL was taken and placed in a 10 mL graduated cylinder and diluted to 4.0 mL, giving a solution with 0.16 mM in dithiolene. This faint green-blue solution was put in a sealable quartz cuvette (1.0 cm pathlength). The cuvette was sealed and a UV-vis spectrum (250-850 nm) was collected. Ethylene was added to the sample by allowing the gas to bubble through the solution for approximately 2 min to saturate the solution. The cuvette was sealed under ethylene. By the time ethylene addition was complete a color change was already evident; the mixture changed from green-blue to yellow-brown. UV-vis spectra (scan range: 250-850 nm) were collected over time after ethylene addition ($T \approx 25^oC$) (see below, Figure S3):

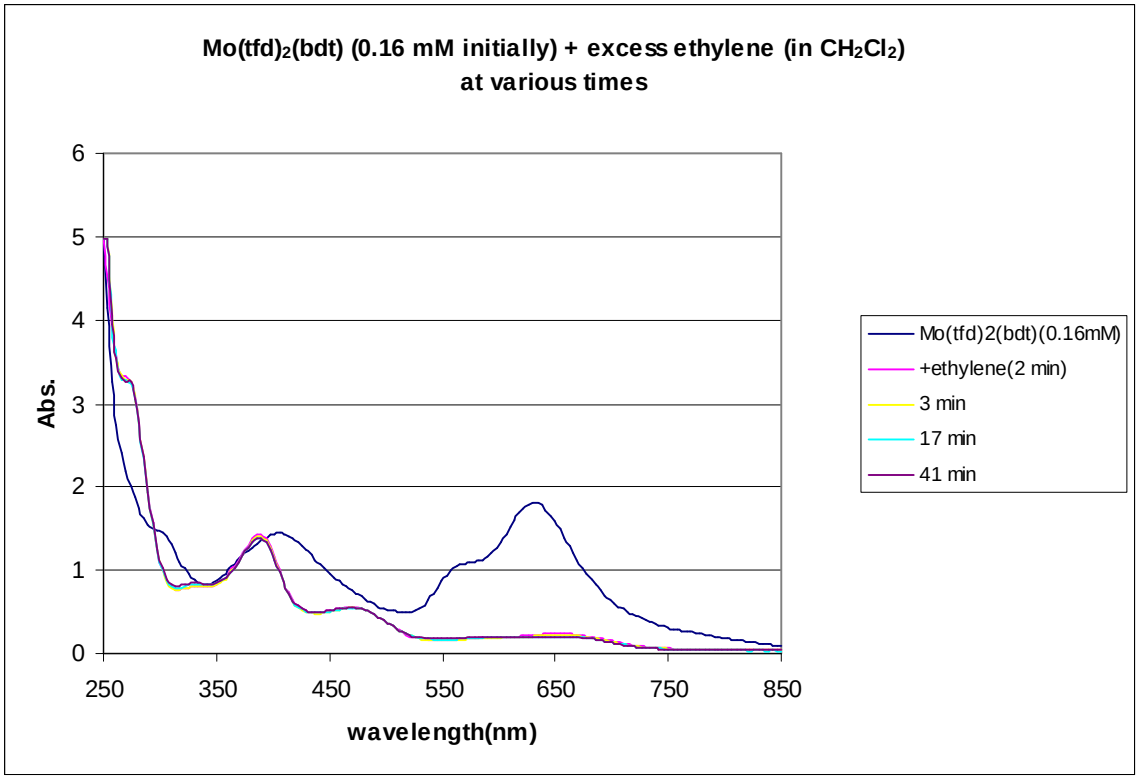

Figure S3. UV-vis spectra (solvent = CH_2Cl_2) monitoring the reaction of $Mo(tfd)_2(bdt)$ (0.16 mM initially) with excess ethylene (saturated CH_2Cl_2 solution) ($T \approx 25^oC$).

Comments: the consumption of $Mo(tfd)_2(bdt)$ was followed by decay of the bands at λ_{max} = 630 nm and λ_{max} = 406 nm. As seen in Fig. S3, the reaction between $Mo(tfd)_2(bdt)$ and ethylene is very rapid (finished within 2 min.), especially compared the reactions of

$Mo(tfd)_3$ or $Mo(bdt)_3$ with ethylene (see above). The product, $Mo(tfd)_2(bdt(CH_2CH_2))$ is characterized by a shoulder at 275 nm and a band at 386 nm (Fig. S3).

Reaction of $Mo(bdt)_2(tfd)$ with excess ethylene (low concentration; monitored by UV-vis). $Mo(bdt)_2(tfd)$ (9.8 mg, 0.0163 mmol) was weighed into a vial and dissolved in 2.0 mL of dichloromethane. From the resulting dark green solution (8.14 mM in $Mo(bdt)_2(tfd)$), 79.0 µL ($6.4x10^{-4}$ mmol) was taken and placed in a graduated cylinder and diluted to 4.0 mL, giving a solution with 0.16 mM in $Mo(bdt)_2(tfd)$. The solution was placed in a sealable quartz cuvette (1.0 cm pathlength). Ethylene was added by allowing the gas to gently bubble through the UV-vis sample for approximately 2 min. The cuvette was sealed under ethylene and UV-vis spectra were collected over time (scan range: 250-850 nm; T ≈ 25°C) (Figure S4, see below):

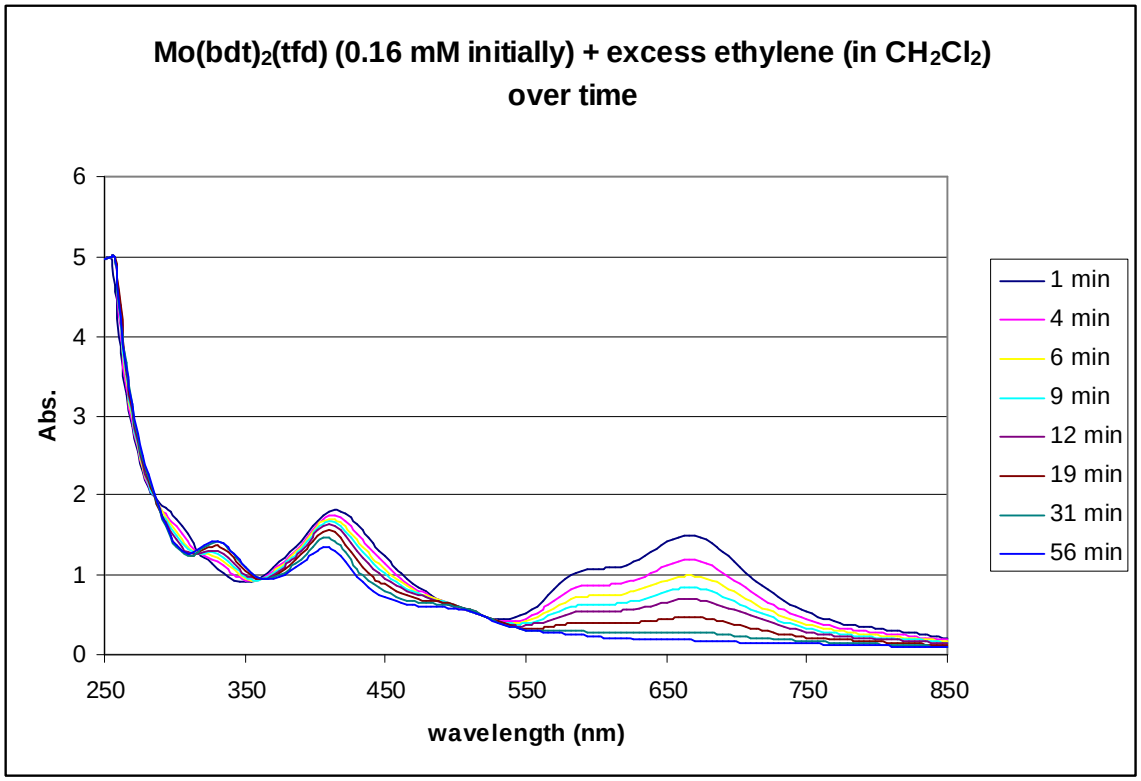

Figure S4. UV-vis spectra (solvent = CH_2Cl_2) monitoring the reaction of $Mo(bdt)_2(tfd)$ (0.16 mM initially) with excess ethylene (saturated CH_2Cl_2 solution) (T ≈ 25°C).

Comments: the consumption of $Mo(bdt)_2(tfd)$ was followed by decay of the bands at λ_{max} = 666 nm and λ_{max} = 418 nm. Under these conditions, $t_{1/2}$ for $Mo(bdt)_2(tfd)$ ≈ 11 min. Thus, reactions of mixed ligand complexes $Mo(bdt)_2(tfd)$ and $Mo(tfd)_2(bdt)$ with ethylene are more rapid than the analogous reactions involving homoleptic $Mo(bdt)_3$ and $Mo(tfd)_3$.

Synthesis of $Mo(tfd)_2(bdt)$. $[NEt_4]_2[MoO(tfd)_2]$ (389 mg, 0.472 mmol) was combined with CH_2Cl_2 (5 mL) (orange solution/suspension). I_2 (60 mg, 0.24 mmol) was added, with an additional 3 mL of CH_2Cl_2 and the color of the solution changed to green-brown (with suspended solid material). The mixture was stirred at RT for 20 min. Benzene-1,2-

dithiol (71 mg, 0.50 mmol) was added in CH_2Cl_2 (1.5 mL x 2 washings), causing the color to change from green-brown to a deeper green. The mixture was stirred at RT for 1.5 h under nitrogen. The volatiles were removed under vacuum to give dark green colored residue. In air: to this residue was added acetone/chloroform (1:1 v/v) (~4 mL) which dissolved most of the dark colored material. The resulting dark green colored solution was placed on a silica gel column (16 g SiO_2, suspended in chloroform, inner column diameter = 1.7 cm). Chloroform (75 mL) was passed through the column which produced (a) colorless eluent and (b) faintly green colored eluent (discarded). The solvent system was changed to acetone/chloroform (1:1 v/v); 30 mL of this solvent mixture produced (a) faintly green colored eluent (discarded). An additional 60 mL of acetone/chloroform (1:1 v/v) gave dark green colored eluent (kept). From the final green colored fraction, the volatiles were removed under vacuum to afford dark green colored residue. In air: this residue was redissolved in CH_2Cl_2 (approximately 3 mL). The solvent/volatiles were again removed under reduced pressure to give 210 mg of dark green colored residue ($[NEt_4][Mo(tfd)_2(bdt)]$, 0.26 mmol). Under inert conditions: to this dark green residue was added chloroform (4 mL), which mostly dissolved the green product. $Mo(tfd)_3$ (210 mg, 0.27 mmol) was added, with an additional 2 mL of chloroform, to the dark green solution. The mixture was stirred under N_2, at 55°C, for 3 h, during which time the color changed to very intense blue-green. Under reduced pressure, the volume of the dark blue-green solution was reduced by approximately half (to ~ 3 mL) and the concentrated solution/suspension was applied to a silica gel column (6-7 g SiO_2 (dried), suspended in hexanes/chloroform (1:1 v/v), inner column diameter = 1.7 cm). Hexanes/chloroform (1:1 v/v) (~ 15 mL) were passed through the column until the blue-green product reached the bottom of the column. The blue-green product was eluted from the column using hexanes/chloroform (1:1 v/v) (~ 20 mL). The solvent/volatiles were removed under vacuum (>2 h under full vacuum, 70°C). The resulting dark blue-green solid was stored under an inert atmosphere (149 mg, 0.22 mmol, 46% based on $[NEt_4]_2[MoO(tfd)_2]$). Anal. Calc. for $C_{14}H_4F_{12}S_6Mo$: C 24.42, H 0.59, S 27.95; Found: C 24.44 , H 0.39, S 28.24. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.64 (m, 2H, $S_2(C_6\underline{H}_4)$), 8.33 (m, 2H, $S_2(C_6\underline{H}_4)$). ^{19}F NMR (470 MHz, $CDCl_3$) δ -56.0 (s, 12F, $(C\underline{F}_3)_2$ x 2). UV-vis (dichloromethane): $\lambda_{max}(\varepsilon)$ = 630 (11000), 580(shoulder)(7000), 406 (9000).

Synthesis of $Mo(bdt)_2(tfd)$. $Mo(bdt)_2(PPh_2Me)_2$ (300 mg, 0.39 mmol) was combined with CH_2Cl_2 (8 mL). 1,2-Bis(trifluoromethyl)dithietene ($S_2C_2(CF_3)_2$) (290 mg, 1.3 mmol) was added to the red-orange solution/suspension in CH_2Cl_2 washings (3 x 1 mL). The mixture was stirred under static N_2 for 2.5 h, at RT (20-25°C), during which time the color of the solution became deep green in color. The solvent/volatiles were removed under vacuum to afford very dark green color amorphous residue. In air: This residue was dissolved in chloroform (approximately 4 mL) and the resulting deep green solution was placed on a silica gel column (16 g SiO_2, suspended in chloroform/hexanes (1:1 v/v), inner column diameter = 1.7 cm). Chloroform/hexanes (1:1 v/v, ~ 25 mL) were passed through the column until the eluent leaving the column was green in color (discarded). More chloroform/hexanes (1:1 v/v, ~ 45 mL) were passed through the column, producing deep green colored eluent (kept). From the green eluent, the solvent/volatiles were removed under reduced pressure (>2 h, 70°C) to give dark green microcrystalline solid

(140 mg, 0.23 mmol, 60% based on $Mo(bdt)_2(PPh_2Me)_2$). Anal. Calc. for $C_{16}H_8F_6S_6Mo$: C 31.89, H 1.34, S 31.93; Found: C 31.46, H 1.53, S 32.42. ^1H NMR (500 MHz, $CDCl_3$) δ 7.50 (m, 4H, $S_2(C_6\underline{H}_4)$ x 2), 8.23 (m, 4H, $S_2(C_6\underline{H}_4)$ x 2). ^{19}F NMR (470 MHz, $CDCl_3$) δ -55.9 (s, 6F, $(C\underline{F}_3)_2$). UV-vis (dichloromethane): $\lambda_{max}(\varepsilon)$ = 666 (11000), 594 (shoulder) (8000), 418 (11000).

X-ray quality crystals were grown by slow evaporation of toluene. See below (Fig. S5) for an alternative view of one molecule from the unit cell ('b'), showing the ligand bending of the dithiolene ligands along the intraligand S···S axes. Ligand bend angles were calculated with PLATON, [7] using least-squares planes through the S-C-C-S units and the corresponding S-Mo-S units.

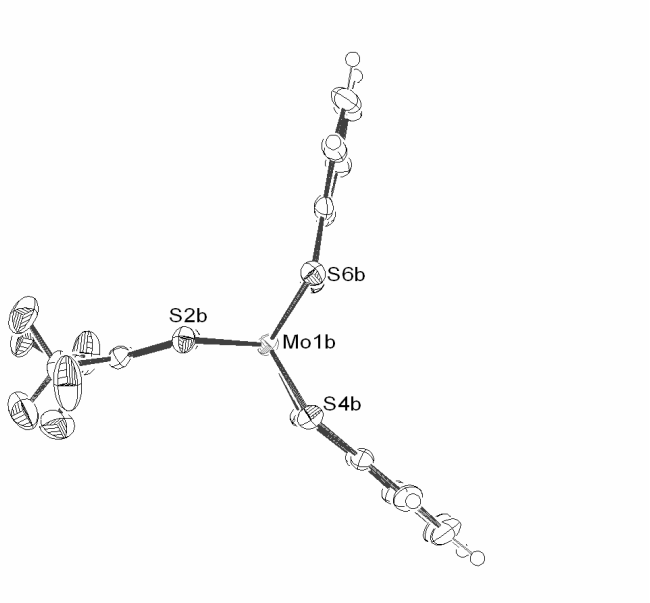

Figure S5. Alternative view of the crystal structure for $Mo(bdt)_2(tfd)$ (50% probability ellipsoids) showing ligand bending along S···S intraligand axes. Toluene solvates not shown.

Comments: Both crystallographically independent molecules of $Mo(bdt)_2(tfd)$ in the unit cell show ligand bending to be more pronounced for the bdt ligand, compared to the tfd ligands. The average (for all four bdt ligands in two molecules) ligand bend angle is 22.4° for the bdt ligands versus an average (for two tfd ligands in two molecules) ligand bend of 17.9° for tfd ligands. This trend supports the assertion that electron-density is concentrated on the more electronegative tfd ligand in $Mo(bdt)_2(tfd)$. The tfd ligand has partial ene-dithiolate character (i.e., fully reduced), while the bdt ligands are partially oxidized; therefore, the ligand π system on the bdt ligands is better suited to interacting with the occupied metal d_{z2} orbital, compared the analogous orbitals on the tfd ligand, which have a higher degree of occupancy.

Synthesis of $Mo(tfd)_2(bdt(CH_2CH_2))$. $Mo(tfd)_2(bdt)$ (0.022 M) with 3,5-bis(trifluoromethyl)bromobenzene (BTBB) (internal standard, 0.041 M) in CD_2Cl_2 was treated with ethylene by allowing the gas to bubble through the NMR sample. ^1H and ^{19}F NMR show the reaction to form $Mo(tfd)_2(bdt(CH_2CH_2))$ to be complete in <15 min. Comparison of product and internal standard integrations shows mass balance to be 83%.

No other products were observed. The missing material is likely accounted for by a small amount of red-brown precipitate in the NMR tube (i.e., $Mo(tfd)_2(bdt(CH_2CH_2))$ is sparingly soluble in chlorinated solvents). ^1H NMR (500 MHz, CD_2Cl_2) δ 2.25 (m, 2H, $(SCH^aH^b)_2$), 2.80 (m, 2H, $(SCH^aH^b)_2$), 5.40 (s, unreacted ethylene), 7.34 (m, 2H, $S_2(C_6H_4)$), 7.59 (m, 2H, $S_2(C_6H_4)$), 7.87 (s, 1H, BTBB), 8.02 (s, 2H, BTBB). ^{19}F NMR (470 MHz, CD_2Cl_2) δ -64.13 (BTBB), -55.3 (s, 6F, $(CF_3^a)_2$), -55.1 (s, 6F, $(CF_3^b)_2$). In a separate experiment, crystals for X-ray analysis were grown by allowing ethylene to slowly diffuse (through a 25G5/8 gauge syringe needle) into a toluene solution of $Mo(tfd)_2(bdt)$ (~0.01 M). Analysis of the data using PLATON[7] revealed that the crystal was a non-merohedral twin, and a twin rotation matrix (1 0 0.005, 0 -1 0, 0 0 -1) was applied. The twin fraction refined to 0.664:0.336(3). The F atoms of two of the CF3 groups are disordered over two sites with refined occupancies 0.58(3):0.42(3) and 0.65(2):0.38(2) for the major and minor components of the atoms F1/F2/F3 and F4/F4/F6, respectively. In addition, there are 1.5 molecules of toluene solvent in the asymmetric unit, one of these molecules lies on an inversion center and is hence disordered by virtue of the crystallographic symmetry.

Ethylene release from $Mo(tfd)_2(bdt(CH_2CH_2))$. A $CDCl_3$ solution of $Mo(tfd)_2(bdt)$ (0.013 M) and BTBB (internal standard, 0.022 M) was treated with ethylene by allowing the gas to bubble through the blue-green solution for ~5 min. The mixture was stirred at RT, under ethylene, for 20 min, during which time the color changed from deep blue-green to dark red-brown (with some insoluble brown-red material visible). The mixture was heated to reflux, under active argon pressure (mineral oil bubbler) for 21 h. During this time, the mixture changed color from dark red-brown to deep blue-green. The mixture was cooled to RT and a portion of the blue-green solution was placed in a J. Young NMR tube for spectroscopic analysis. Product concentrations were obtained by comparison of their ^1H integrations with those of 3,5-bis(trifluoromethyl)bromobenzene (internal standard). ^1H and ^{19}F NMR show free $Mo(tfd)_2(bdt)$ (5.1 mM, 41% of original concentration), $Mo(tfd)_2(bdt(CH_2CH_2))$ (4.6 mM), and 2,3-dihydro-1,4-benzodithiin ($bdt(CH_2CH_2)$) (1.5 mM). Mass balance was 87%. The missing material is probably explained by the low solubility of $Mo(tfd)_2(bdt(CH_2CH_2))$ or by the presence of paramagnetic products. 2,3-dihydro-1,4-benzodithiin was identified by its ^1H NMR spectrum. ^1H NMR (500 MHz, $CDCl_3$) (for dihydrodithiin only; see above for spectral assignments for $Mo(tfd)_2(bdt)$ and $Mo(tfd)_2(bdt(CH_2CH_2))$ δ 3.27 (s, 4H, CH_2CH_2), 7.00 (m, 2H, $S_2(C_6H_4)$), 7.16 (m, 2H, $S_2(C_6H_4)$).

Synthesis of $Mo(bdt)(tfd)(bdt(CH_2CH_2))$ for characterization by elemental analysis. $Mo(bdt)_2(tfd)$ (100 mg, 0.17 mmol) was combined with hexanes (5-6 mL) in a 50 mL pyrex reaction vessel. To this green mixture, ethylene was added by allowing the gas to bubble through the hexanes/$Mo(bdt)_2(tfd)$ solution/suspension for ~5 min. The vessel was sealed under ethylene and the mixture was allowed to react at RT (protected from light) for 21 h. After overnight reaction, the green color associated with $Mo(bdt)_2(tfd)$ had disappeared. The product, $Mo(bdt)(tfd)(bdt(CH_2CH_2))$, was visible as brown-red precipitate in a red-brown supernatant solution. The brown-red solid was recovered by filtration and washed with hexanes (1 mL x 3) and dried in vacuo (86 mg, 80%). Anal. Calc. for $C_{18}H_{12}F_6S_6Mo$: C 34.28, H 1.92, S 30.51; Found: C 33.96, H 1.68, S 30.43.

Observation of Mo(bdt)(tfd)(bdt(CH_2CH_2)) by NMR spectroscopy. A CD_2Cl_2 solution of Mo(bdt)$_2$(tfd) (0.020 M), with 3,5-bis(trifluoromethyl)bromobenzene (BTBB, internal standard, 0.028 M) was placed in a J. Young NMR tube and treated with ethylene by allowing the gas to gently bubble through the solution for ~2 min. The NMR tube was sealed under ethylene. The mixture was allowed to react at RT for ~30 min and an NMR spectrum was collected. Product concentrations were obtained by comparison of their ^{1}H integrations with those of 3,5-bis(trifluoromethyl)bromobenzene (internal standard): Mo(bdt)$_2$(tfd) (3.8 mM, 19% of original concentration), Mo(bdt)(tfd)(bdt(CH_2CH_2)) (two diastereomers, 6.3 mM), 2,3-dihydro-1,4-benzodithiin (bdt(CH_2CH_2), 2.2 mM). Mass balance is 62%; the missing material is likely accounted for by the low solubility of the alkene adducts. ^{1}H NMR (500 MHz, CD_2Cl_2) δ 2.17-2.28 (ov m, C$\underline{H}^a$HC$\underline{H}^a$H, two diastereomers), 2.62-2.80 (ov m, CH$\underline{H}^b$CH$\underline{H}^b$, two diastereomers), 3.25 (s, dihydrodithiin C$\underline{H}_2$C$\underline{H}_2$), 5.39 (s, unreacted ethylene), 6.77 (m, (Mo(bdt)(tfd))$_x$), 6.92 (m, (Mo(bdt)(tfd))$_x$), 6.98 (m, dihydrodithiin S_2(C$_6\underline{H}_4$)), 7.01-7.07 (ov m, (Mo(bdt)(tfd))$_x$)), 7.13 (m, dihydrodithiin S_2(C$_6\underline{H}_4$)), 7.16-7.46 (ov m, (Mo(bdt)(tfd))$_x$) and Mo(bdt)(tfd)(bdt(CH_2CH_2))), 7.49-7.59 (ov m, Mo(bdt)(tfd)(bdt(CH_2CH_2) and unreacted Mo(bdt)$_2$(tfd)), 7.86 (s, BTBB), 8.01 (s, BTBB), 8.05-8.12 (ov m, (Mo(bdt)(tfd))$_x$), 8.17 (m, (Mo(bdt)(tfd))$_x$), 8.25 (m, unreacted Mo(bdt)$_2$(tfd)). ^{19}F NMR (470 MHz, CD_2Cl_2) -64.13 (s, BTBB), -57.4 to -56.1 (ov m, (Mo(bdt)(tfd))$_x$), -56.0 (s, unreacted Mo(tfd)$_2$(bdt)), -55.9 to -55.3 (ov m, (Mo(bdt)(tfd))$_x$), -55.0 (s, Mo(bdt)(tfd)(bdt(CH_2CH_2)), one of two diastereomers), -54.8 (s, Mo(bdt)(tfd)(bdt(CH_2CH_2)), one of two diastereomers).

Comments: the alkene adducts (two possible diastereomers, depending on which side of bdt ligand is attacked by ethylene) Mo(bdt)(tfd)(bdt(CH_2CH_2)) are only sparingly soluble in chlorinated and aromatic NMR solvents (e.g., $CDCl_3$, CD_2Cl_2, toluene-d_8). In more strongly coordinating solvents (acetone-d_6, acetonitrile-d_3, THF-d_8), the metal 2,3-dihydro-1,4-benzodithiin is displaced and metal decomposition products are observed as a manifold of ^{1}H and ^{19}F signals, for ill-defined (presumably oligomeric ((Mo(bdt)(tfd))$_x$). In $CDCl_3$ and CD_2Cl_2, weak signals for Mo(bdt)(tfd)(bdt(CH_2CH_2)) can be observed, and minor amounts of decomposition products (dihydrodithiin and (Mo(bdt)(tfd))$_x$) are formed as the adduct forms in situ, upon reaction of Mo(bdt)$_2$(tfd) and ethylene. Most of the product precipitates from solution in the form of brown-red microcrystals in weakly donating solvents. For preparative purposes, aliphatic solvents (e.g., hexanes) are ideal (see above), where the alkene adduct precipitates from solution in the form of brown-red microcrystals and the decomposition pathway is suppressed.

Decomposition of Mo(bdt)(tfd)(bdt(CH_2CH_2)) in CD_3CN. Mo(bdt)(tfd)(bdt(CH_2CH_2)) (6.1 mg, 0.010 mmol), isolated as described above, was combined with CD_3CN, which dissolved the solid and gave a red-brown colored mixture. The mixture was left at RT for ~ 15 min before analysis by ^{1}H and ^{19}F NMR spectroscopy. The NMR spectra show the only products to be 1,4-benzo-2,3-dihydro-1,4-dithiin (bdt(CH_2CH_2) and metal decomposition products ((Mo(bdt)(tfd))$_x$). The metal decomposition products appear as a large number of overlapping, low-intensity multiplets in the ^{1}H and ^{19}F spectra (not reported here, see above for representative data). No alkene adducts (Mo(bdt)(tfd)(bdt(CH_2CH_2))) were observed (i.e., dissociation of dihydrodithiin

from metal is quantitative in this coordinating solvent). ^{1}H NMR (500 MHz, CD_3CN, dihydrodithiin only) δ 3.26 (s, 4H, dihydrodithiin $C\underline{H}_2C\underline{H}_2$), 7.01 (m, 2H, dihydrodithiin $S_2(C_6H_4)$), 7.14 (m, 2H, dihydrodithiin $S_2(C_6H_4)$).

Synthesis of $[NEt_4]_2[Mo(bdt)(mnt)(tfd)]$. $Mo(bdt)_2(tfd)$ (99 mg, 0.16 mmol) was combined with hexanes (4-5 mL) in a 50 mL pyrex reaction vessel (sealable with a Teflon valve), giving a green solution with some suspended $Mo(bdt)_2(tfd)$. Ethylene was introduced by allowing the gas to bubble through the hexanes/$Mo(bdt)_2(tfd)$ solution for 5 min to saturated the solution/atmosphere inside the vessel. The mixture was sealed under ethylene and allowed to react at RT, with stirring (protected from light), overnight (approximately 20 h). After overnight reaction, the green color associated with $Mo(bdt)_2(tfd)$ had disappeared to give faintly violet colored supernatant solution with suspended fine brown-red solid material. From this mixture, the solvent/volatiles were removed under vacuum to afford brown solid residue. In air: To the brown residue was added $Na_2S_2C_2(CN)_2$ (61 mg, 0.33 mmol) in water/CH_3CN (1:1 v/v, 2.5 mL x 2 washings), giving, initially, a brown solution/suspension. The mixture was stirred at 70^{o}C for 1 h, during which time a deep green colored homogeneous solution developed. Under vacuum, the volume of the solution was reduced by half (to ~ 2-3 mL). To this mixture was added NEt_4Br (168 mg, 0.80 mmol) in 1.5 mL of water, which immediately caused dark colored oily solid to precipitate. The oily solid was recovered (in air) by filtration. The solid product was washed with water (1 mL x 5), ethanol (1 mL x 5) and diethyl ether (1 mL x 10), which caused the product to become a tractable fine powder. The solid was dried in vacuo (dark blue powder, 92 mg, 67% based on $Mo(bdt)_2(tfd)$).
Anal. Calc. for $C_{30}H_{44}F_6S_6N_4Mo_1$: C 41.75, H 5.14, N 6.49, S 22.29; Found: C 41.50, H 5.40, N 6.02, S 22.84. ^{1}H NMR (500 MHz, acetone-d_6) δ 1.16 (m, 24H, $N^+(CH_2C\underline{H}_3)_4$ x 2), 3.13 (q, J_{HH} = 7.3 Hz, 16H, $N^+(C\underline{H}_2Me)_4$ x 2), 6.79 (m, 2H, $S_2(C_6\underline{H}_4)$), 7.52 (m, 2H, $S_2(C_6\underline{H}_4)$). ^{19}F NMR (470 MHz, acetone-d_6) δ -53.5 (s, 6F, $(CF_3)_2$). X-ray quality crystals were grown by slow diffusion of diethyl ether vapor into an acetone solution of $[NEt_4]_2[Mo(bdt)(mnt)(tfd)]$. The crystal structure contains one tetraethylammonium [TEA] cation lying on a general position in the unit cell. During the refinement, areas of electron density were located in difference Fourier maps (on inversion centers) that were assigned as two additional [0.5 occupancy] tetraethylammonium cation molecules. The peak pattern of electron density illustrated that these molecules were highly disordered about the inversion centers. Attempts to model the disorder were unsuccessful. In the final cycles of refinement, the contribution to electron density corresponding to the disordered molecules was removed from the observed data using the SQUEEZE option in PLATON.[7] The resulting data vastly improved the precision of the geometric parameters of the remaining structure. The contribution of an additional molecule of TEA has been included in the molecular formula. The presence of two molecules of TEA in the molecular formula is confirmed by the charge balance and the other chemical analyses. A thermal ellipsoid plot for $[Mo(bdt)(mnt)(tfd)]^{2-}$ is shown in Figure S6 (a) below, along with selected distances and angles.

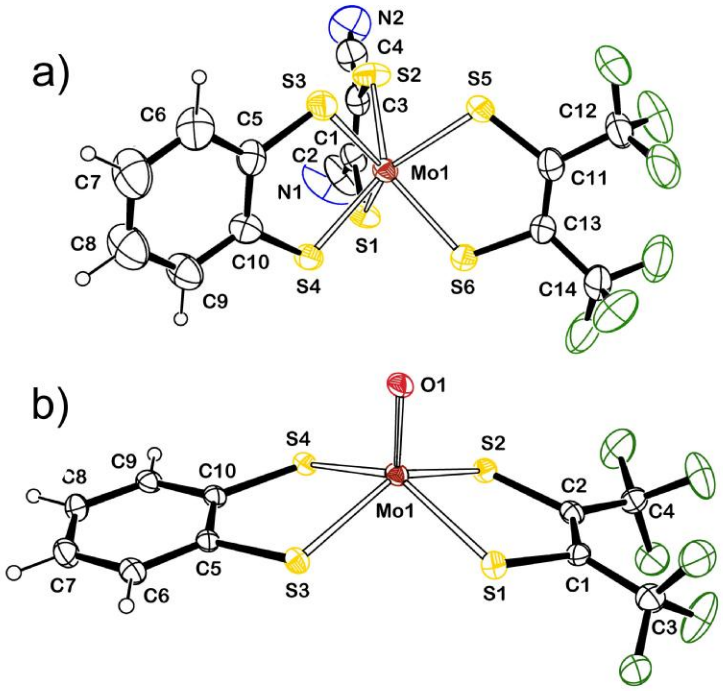

Figure S6. X-ray crystal structures of (a) $[Mo(bdt)(tfd)(mnt)]^{2-}$ and (b) $[MoO(bdt)(tfd)]^{2-}$, shown using 30% probability ellipsoids. Tetraethylammonium counterions (partially disordered for (a), well-behaved for (b) not shown. For (b), one rotational orientation of the disordered trifluoromethyl group involving C3 is shown. Selected distances and angles: (a) $[Mo(bdt)(tfd)(mnt)]^{2-}$: Mo1-S1, 2.394(2); Mo1-S2, 2.397(2); Mo1-S3, 2.382(1); Mo1-S4, 2.379(1); Mo1-S5, 2.384(1); Mo1-S6, 2.371(1); S1-Mo1-S2, 80.80(6); S3-Mo1-S4, 80.95(5); S5-Mo1-S6, 80.32(5); ligand bend of bdt, tfd, mnt, 2.7(2), 0.1(2), 0.5(2), respectively. (b) $[O=Mo(bdt)(tfd)]^{2-}$: Mo1-S1, 2.383(1); Mo1-S2, 2.380(1); Mo1-S3, 2.389(1); Mo1-S4, 2.378(1); Mo1-O1, 1.702(3); S1-Mo1-S2, 82.62(4); S3-Mo1-S4, 83.26(4); ligand bend angles of bdt and tfd, 17.8(1) and 14.2(1), respectively.

Synthesis of $[NEt_4]_2[MoO(bdt)(tfd)]$. $Mo(bdt)_2(tfd)$ (70 mg, 0.12 mmol) was combined with hexanes (4-5 mL) in a 50 mL pyrex reaction vessel, giving a green solution with some suspended $Mo(bdt)_2(tfd)$. Ethylene was introduced by allowing the gas to bubble through the hexanes/$Mo(bdt)_2(tfd)$ solution for 5 min to saturated the solution/atmosphere inside the vessel. The mixture was sealed under ethylene and allowed to react, with stirring (protected from light), overnight (approximately 20 h). After overnight reaction, the green color associated with $Mo(bdt)_2(tfd)$ had disappeared to give faintly violet colored supernatant solution with suspended fine brown-red solid material. From this mixture, the solvent/volatiles were removed under vacuum to afford brown solid residue. Note: the following manipulations were done under anaerobic (argon) (but not anhydrous) conditions. NEt_4OH (0.13 mL of 35% w/w solution in water, 0.30 mmol) was added to the brown solid residue with EtOH (deoxygenated with argon purge) washings (1.5 mL x 2). Initially, a brown-red suspension was observed. The mixture was stirred at RT for 15 min and then heated at 50°C for 35 min. During this time, dark colored precipitate formed and the supernatant solution developed a faint blue color. The mixture was cooled to RT and the volatiles were removed under reduced pressure to afford crude product as a blue solid residue. Under inert (O_2/H_2O free) conditions: to the

blue solid residue was added acetonitrile (2 mL), which mostly dissolved the solid, giving a blue solution. This solution was filtered. To the filtered solution was added THF (2 mL) and diethyl ether (3 mL). The resulting mixture was cooled overnight (~19 h), during which time pure product precipitated from the blue solution in the form of red-brown microcystals. The red-brown solid was recovered by filtration. The solid was washed with (a) EtOH/THF (1:1 v/v, 1 mL x 5) and (b) diethyl ether (1 mL x 4) and then dried under vacuum. Yield: 57 mg, 67% based on $Mo(bdt)_2(tfd)$. Anal. Calc. for $C_{26}H_{44}F_6S_4N_2OMo_1$: C 42.26, H 6.01, N 3.79, S 17.36; Found: C 42.25, H 5.77, N 3.63, S 17.86. ^{1}H NMR (500 MHz, CD_3CN) δ 1.07 (m, 24H, $N^+(CH_2C\underline{H}_3)_4$ x 2), 2.99 (q, J_{HH} = 7.3 Hz, 16H, $N^+(C\underline{H}_2Me)_4$ x 2), 6.76 (m, 2H, $S_2(C_6\underline{H}_4)$), 7.50 (m, 2H, $S_2(C_6\underline{H}_4)$). ^{19}F NMR (470 MHz, CD_3CN) δ -53.8. X-ray quality crystals were grown by vapor diffusion of THF into a CH_3CN solution of a $[NEt_4]_2[MoO(bdt)(tfd)]$ (red-orange plates). A thermal ellipsoid plot for $[MoO(bdt)(tfd)]^{2-}$ is shown in Figure S6 (b) above, along with selected distances and angles.

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