Supplementary Information:

Behavior of anionic molybdenum(IV, VI) and tungsten(IV, VI) complexes containing bulky hydrophobic dithiolate ligands and intramolecular NH···S hydrogen bonds in nonpolar solvents

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Synthesis of ligand precursors.

(4-^{t}BuC$_6$H$_4$)$_3$CCOCl. A suspension of (4-^{t}BuC$_6$H$_4$)$_3$CCOOH (8.88 g, 19.5 mmol) in SOCl$_2$ (60 mL, 0.84 mol) was refluxed for 1.5 h to afford a yellow solution. After removing volatile materials, the white residue was suspended in CH$_2$Cl$_2$ and concentrated to dryness under reduced pressure with heating. This procedure was repeated for several times to remove completely the residual SOCl$_2$. The resulting white powder was recrystallized from CH$_2$Cl$_2$/n-hexane to afford colorless blocks. Yield: 9.29 g, quant. Mp: 235 °C. Anal. Calcd for C$_{32}$H$_{39}$ClO: C, 80.90; H, 8.27; Cl, 7.46. Found: C, 80.69; H, 8.23; Cl, 7.58.[‡] ^{1}H NMR (CDCl$_3$): δ 7.32 (d, J = 8.9 Hz, 6H, Ar), 7.25 (d, J = 8.9 Hz, 6H, Ar), 1.31 (s, 27H, ^{t}Bu). IR (KBr): 1795, 1768 ($\nu_{C=O}$) cm^{-1}.

[‡]The chlorine (Cl) content in (4-^{t}BuC$_6$H$_4$)$_3$CCOCl was analyzed by the silver absorption method with an elemental analyzer (Yanaco New Science Inc.).

(4-^{t}BuC$_6$H$_4$)$_3$CCONHPh. A solution of (4-^{t}BuC$_6$H$_4$)$_3$CCOCl (136 mg, 285 μmol) in CH$_2$Cl$_2$ (4 mL) was added to a mixture of aniline (27.7 mg, 297 μmol) and Et$_3$N (29.8 mg, 294 mmol) in CH$_2$Cl$_2$ (3 mL) at 0 °C, and the reaction mixture was stirred at 0 °C for 17 h to afford a colorless solution. After removing volatile materials, the resulting white residue was extracted with AcOEt and washed successively with water, sat. NaCl aq., 2% HCl aq., sat. NaCl aq., 4% NaHCO$_3$ aq., and sat. NaCl aq. The organic layer was dried over Na$_2$SO$_4$, filtered, and concentrated to dryness to afford colorless solid. Recrystallization from AcOEt/n-hexane gave colorless needles. Yield: 285 mg, quant. Mp: 241 °C (dec.). Anal. Calcd for C$_{38}$H$_{45}$NO: C, 85.83; H, 8.53; N, 2.63. Found: C, 85.72; H, 8.54; N, 2.62. ^{1}H NMR (CDCl$_3$): δ 7.49 (s, 1H, NH), 7.42 (d, J = 7.9 Hz, 2H, Ph), 7.32 (d, J = 8.7 Hz, 6H, Ar), 7.28 (t, J = 7.9 Hz, 2H, Ph), 7.22 (d, J = 8.7 Hz, 6H, Ar), 7.08 (t, J = 7.9 Hz, 1H, Ph), 1.31 (s, 27H, ^{t}Bu). IR (10 mM in CH$_2$Cl$_2$): 3403 (ν_{NH}), 1683 ($\nu_{C=O}$) cm^{-1}.

(^{n}Bu$_4$N)$_2$[3,6-(NH$_2$)$_2$C$_6$H$_2$-1,2-(SSO$_3$)$_2$]. To a mixture of 3,6-(NH$_2$)$_2$C$_6$H$_2$-1,2-(SSO$_3$K)$_2$ (6.04 g, 14.8 mmol) and ^{n}Bu$_4$NCl (8.24 g, 29.7 mmol) were added water (~30 mL) and CH$_2$Cl$_2$ (~20 mL). The organic layer was separated, and then the remnant product was extracted from aqueous layer with CH$_2$Cl$_2$ (50 mL and 2 × 10 mL). The combined organic layer was washed with water (3 × 5 mL), dried over Na$_2$SO$_4$, and concentrated to dryness under reduced pressure. The green residue was recrystallized from acetone/THF to afford greenish yellow blocks. Yield: 9.19 g, 76%. Mp: 148 °C (dec.). Anal. Calcd for C$_{38}$H$_{78}$N$_4$O$_6$S$_4$·H$_2$O: C, 54.77; H, 9.68; N, 6.72. Found: C, 54.98; H, 9.46; N, 6.77. ^{1}H NMR (CDCl$_3$): δ 6.58 (s, 2H, 4,5-H), 4.50 (br, 4H, NH$_2$), 3.13 (m, 16H, ^{n}Bu$_4$N$^+$), 1.59 (m, 16H, ^{n}Bu$_4$N$^+$), 1.43 (m, 16H, ^{n}Bu$_4$N$^+$), 0.98 (t, J = 7.3 Hz, 24 H, ^{n}Bu$_4$N$^+$). IR (KBr): 3436, 3338 (ν_{NH}), 1017 (ν_{SO}) cm^{-1}.

(^{n}Bu$_4$N)$_2$[3,6-{(4-^{t}BuC$_6$H$_4$)$_3$CCONH}$_2$C$_6$H$_2$-1,2-(SSO$_3$)$_2$]. A solution of (4-^{t}BuC$_6$H$_4$)$_3$CCOCl (4.95 g, 10.4 mmol) in CH$_2$Cl$_2$ (37 mL) was added to a mixture of (^{n}Bu$_4$N)$_2$[3,6-(NH$_2$)$_2$C$_6$H$_2$-1,2-(SSO$_3$)$_2$] (4.08 g, 5.01 mmol) and Et$_3$N (2.8 mL, 20 mmol) in CH$_2$Cl$_2$ (10 mL) at 0 °C, and the

reaction mixture was stirred at 0 °C for 15 h to afford a yellow solution. After removing volatile materials, the yellow residue was washed with water and AcOEt, and then dried under reduced pressure to afford white powder. Recrystallization from hot AcOEt gave colorless blocks. Yield: 8.15 g, 96%. Mp: 251 °C (dec.). Anal. Calcd for $C_{102}H_{154}N_4O_8S_4 \cdot H_2O$: C, 71.62; H, 9.19; N, 3.28. Found: C, 71.52; H, 9.14; N, 3.32. ^{1}H NMR ($CDCl_3$): δ 9.71 (s, 2H, NH), 8.18 (s, 2H, 4,5-H), 7.28 (d, J = 9.0 Hz, 12H, Ar), 7.25 (d, J = 9.0 Hz, 12H, Ar), 3.04 (m, 16H, $^nBu_4N^+$), 1.51 (m, 16H, $^nBu_4N^+$), 1.30 (m, 16H, $^nBu_4N^+$), 1.30 (s, 54H, ^tBu), 0.87 (t, J = 7.3 Hz, 24H, $^nBu_4N^+$). IR (KBr): 3298 (ν_{NH}), 1669 ($\nu_{C=O}$), 1018 (ν_{SO}) cm^{-1}.

Structural determination. Each single crystal of **L1**·3.1CH$_3$OH·H$_2$O, **1-Mo**·8(toluene), **1-Mo**·toluene·5CH$_3$CN, **1-W**·4(toluene)·3CH$_3$CN·H$_2$O, **2-Mo**·5CH$_3$CN and **2-W**·5CH$_3$CN was selected carefully and mounted on MicroMount™ 200 μm with Nujol, which was frozen immediately in a stream of cold nitrogen at 200 K. Data collection was made on a Rigaku RAPID II Imaging Plate area detector with Mo-Kα radiation (0.71075 Å) using MicroMax-007HF microfocus rotating anode X-ray generator and VariMax-Mo optics. The structures were solved by direct methods (SIR2008[1] for **L1**·3.1CH$_3$OH·H$_2$O, SHELX-97[2] for **1-Mo**·8(toluene), **2-Mo**·5CH$_3$CN and **2-W**·5CH$_3$CN, and SIR97[3] for **1-Mo**·toluene·5CH$_3$CN, **1-W**·4(toluene)·3CH$_3$CN·H$_2$O) and expanded Fourier techniques using SHELXL-2014/6.[2] Crystallographic data are shown in Tables S1 and S2. The details of the refinements were embedded in to the CIF.

Table S1 Crystallographic Data for **L1**

	L1·3.1CH$_3$OH·H$_2$O
empirical formula	C$_{73.1}$H$_{96.4}$N$_2$O$_{6.1}$S$_3$
formula weight	1193.94
color	yellow
crystal system	monoclinic
a, Å	25.228(9)
b, Å	20.296(6)
c, Å	14.423(5)
β, deg	103.207(13)
V, Å^3	7190(4)
space group	*C*2
Z	4
D$_{calc}$, g/cm^3	1.103
F (000)	2577
μ(MoK*α*), mm^{-1}	0.152
scan type	ω
2θ$_{max}$, deg	50
No. of reflections unique	11821
No. variables	805
residuals;	0.1461,
*R*1^a (I > 2σ(I)),w*R*2^b (all data)	0.4201
GOF	1.047

$^a R1 = \Sigma||F_o| - |F_c|| / \Sigma|F_o|.$ $^b wR2 = \{\Sigma[w(F_o{}^2 - F_c{}^2)^2] / \Sigma[w(F_o{}^2)^2]\}^{1/2}$
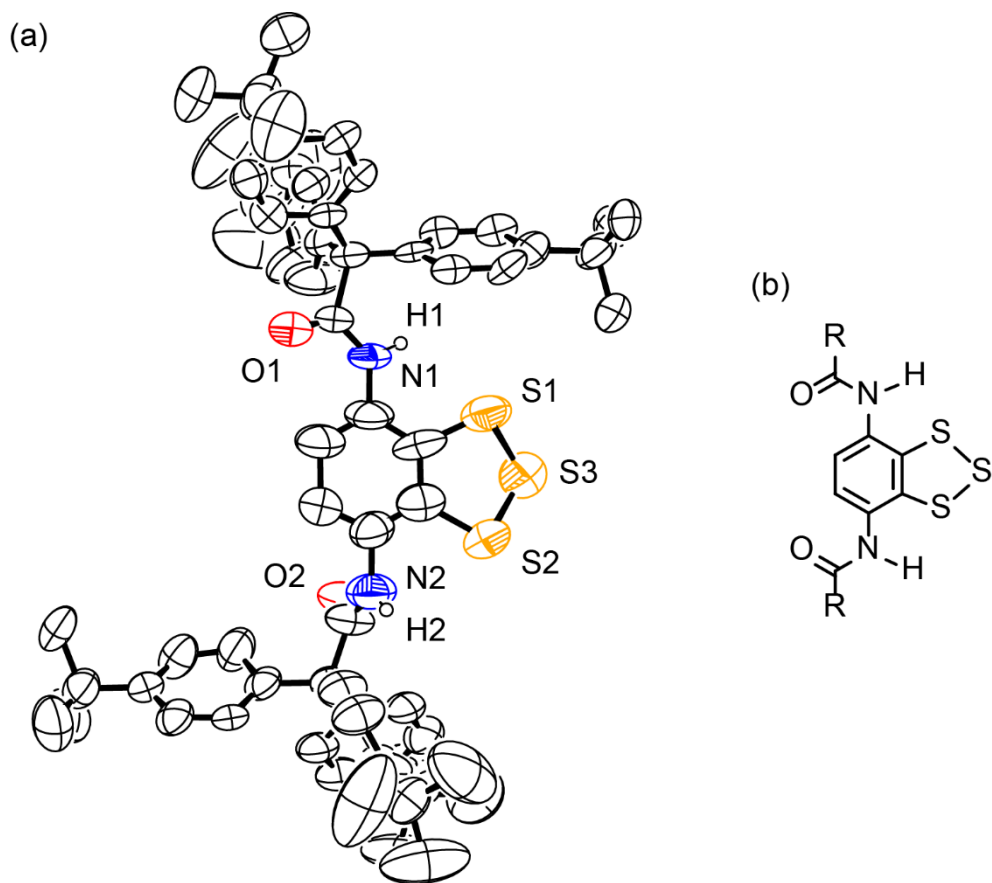
Fig. S1 (a) ORTEP drawing at 50% probability (protons are omitted for clarity except amide groups) and (d) simplified structure of **L1**·3.1CH$_3$OH·H$_2$O.
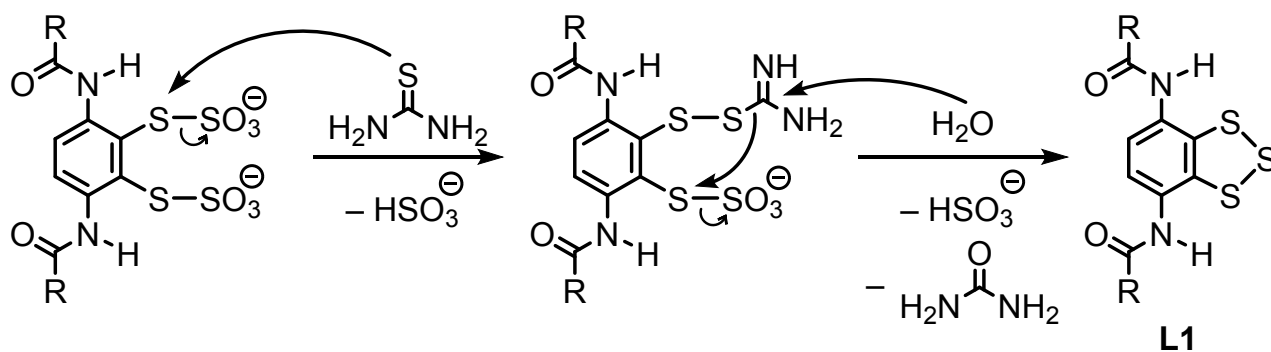
Scheme S1 Proposed Mechanism Producing **L1**

Table S2 Crystallographic Data for **1-Mo**, **1-W**, and **2-W**

	1-Mo·8(toluene)	**1-Mo**· toluene·5CH$_3$CN	**1-W**·4(toluene)· 3CH$_3$CN·H$_2$O
empirical formula	C$_{212}$H$_{268}$MoN$_6$O$_5$S$_4$	C$_{173}$H$_{227}$MoN$_{11}$O$_5$S$_4$	C$_{190}$H$_{247}$N$_9$O$_6$S$_4$W
formula weight	3204.49	2764.82	3065.19
color	yellow	green	orange
crystal system	triclinic	monoclinic	monoclinic
a, Å	16.140(4)	39.1189(16)	39.235(5)
b, Å	18.083(4)	23.7467(11)	23.938(3)
c, Å	18.963(4)	20.0641(14)	20.131(3)
α, deg	116.758(6)		
β, deg	91.907(8)	107.993(8)	108.061(5)
γ, deg	99.703(8)		
V, Å^3	4833.6(18)	17726.9(18)	17976(4)
space group	$P1$	$C2/c$	$C2/c$
Z	1	4	4
D_{calc}, g/cm^3	1.101	1.036	1.133
F (000)	1728	5952	6544
μ(MoKα), mm^{-1}	0.166	0.172	0.744
scan type	ω	ω	ω
2θ$_{max}$, deg	50	50	50
No. of reflections unique	28442	15566	15799
No. variables	2017	1037	929
residuals; $R1^a$ (I > 2σ(I)), w$R2^b$ (all data)	0.0931, 0.2819	0.1148, 0.3668	0.1265, 0.3323
GOF	1.032	1.274	1.109

$^a R1 = \Sigma||F_o| - |F_c|| / \Sigma|F_o|$. $^b wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma[w(F_o^2)^2]\}^{1/2}$

	2-Mo·5CH$_3$CN	**2-W**·5CH$_3$CN
empirical formula	C$_{166}$H$_{219}$MoN$_{11}$O$_6$S$_4$	C$_{166}$H$_{219}$N$_{11}$O$_6$S$_4$W
formula weight	2688.81	2776.72
color	reddish-brown	reddish-orange
crystal system	orthorhombic	orthorhombic
a, Å	14.4864(14)	14.503(2)
b, Å	25.173(3)	25.170(5)
c, Å	21.753(2)	21.806(4)
V, Å^3	7932.6(14)	7960(3)
space group	*Pnn*2	*Pnn*2
Z	2	2
D_{calc}, g/cm^3	1.126	1.158
F (000)	2892	2956
μ(MoKα), mm^{-1}	0.191	0.834
scan type	ω	ω
2θ$_{max}$, deg	50	50
No. of reflections unique	13942	13726
No. variables	767	804
residuals; $R1^a$ (I > 2σ(I)), w$R2^b$ (all data)	0.2043, 0.5205	0.1164, 0.3496
GOF	1.463	1.035
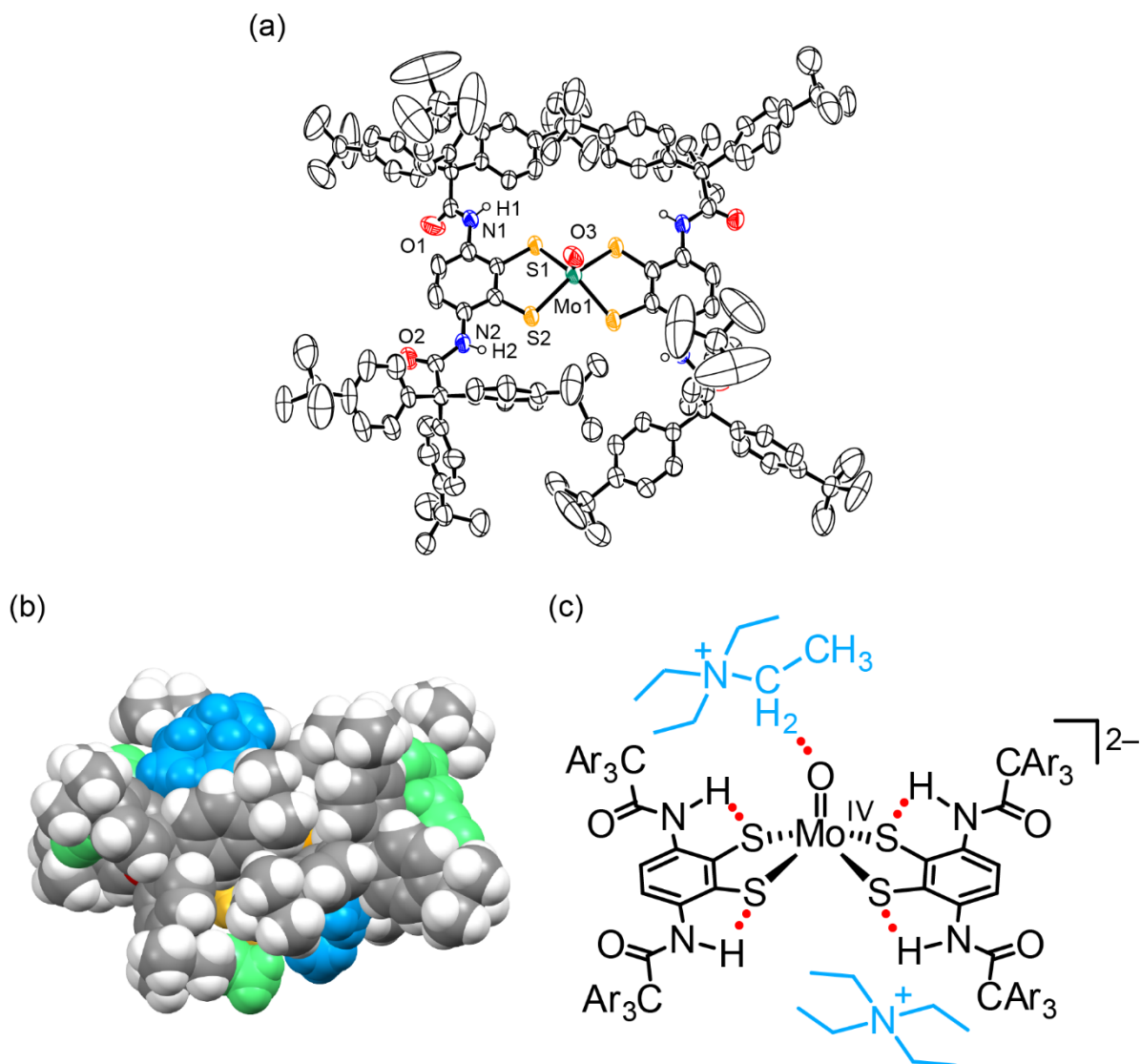
Fig. S2 (a) ORTEP drawing at 50% probability (anion part, protons are omitted for clarity except amide groups) and (b) space-filling model of **1-Mo**·toluene·5CH$_3$CN with Et$_4$N$^+$ (blue), toluene (yellow), and acetonitrile (light green). (c) Schematic drawing of interionic CH···O=Mo hydrogen bond in the crystal.
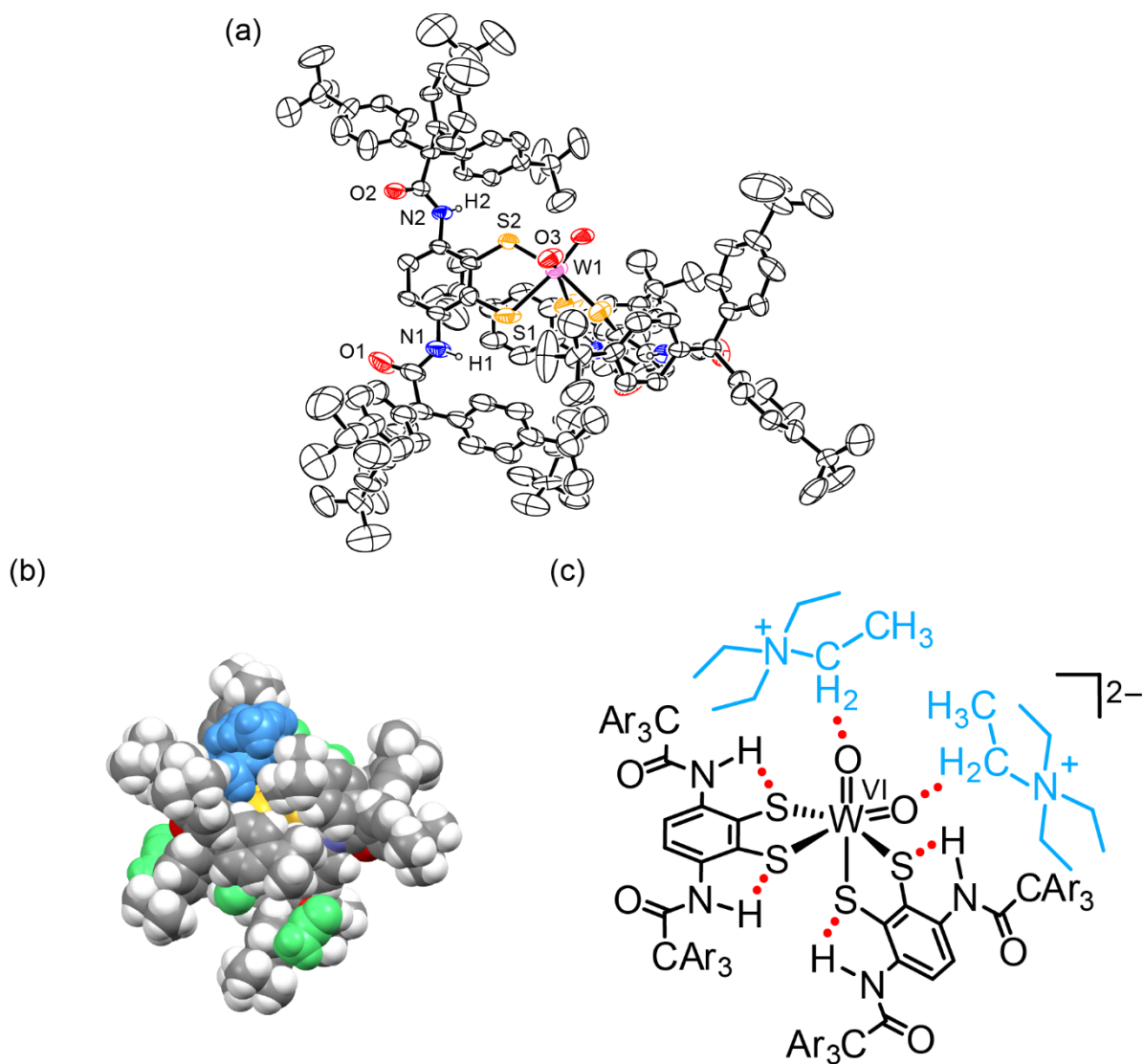
Fig. S3 (a) ORTEP drawing of **2-W**·5CH₃CN at 30% probability (anion part, protons are omitted for clarity except amide groups) and (b) space-filling model with Et₄N⁺ (blue) and acetonitrile (light green). (c) Schematic drawing of the hydrogen bonds in the crystal.

Table S3 Comparison of Selected Bonds and Angles (Å, deg) for the Dioxotungsten(VI) Complexes **2-W** and **4-W**

	2-W	4-W
W=O	1.76(2)	1.735(4)
W–S (*trans*)	2.598(8)	2.607(3)
W–S (*cis*)	2.428(5)	2.426(4)
W–S (mean)	2.51	2.52
Δ(W–S)	0.17	0.18
NH⋯S[a] (*trans*)	2.45	2.47
NH⋯S (*cis*)	2.65	2.74
NH⋯π[a] (*trans*)	3.10	—[b]
NH⋯π (*cis*)	2.78	2.74[c]
dihedral angle[d] (*trans*)	8(5)	7.9(9)
dihedral angle (*cis*)	44(3)	49.7(8)

[a]Hydrogen atoms are located at the calculated positions. Distance between the amide proton and the centroid of the closest benzene ring. [b]No NH⋯π interaction. [c]Intermolecular NH⋯π interaction. [d]Dihedral angle between benzene ring and amide CONH plane (C17-N1-C16-C15 for **2-W**).
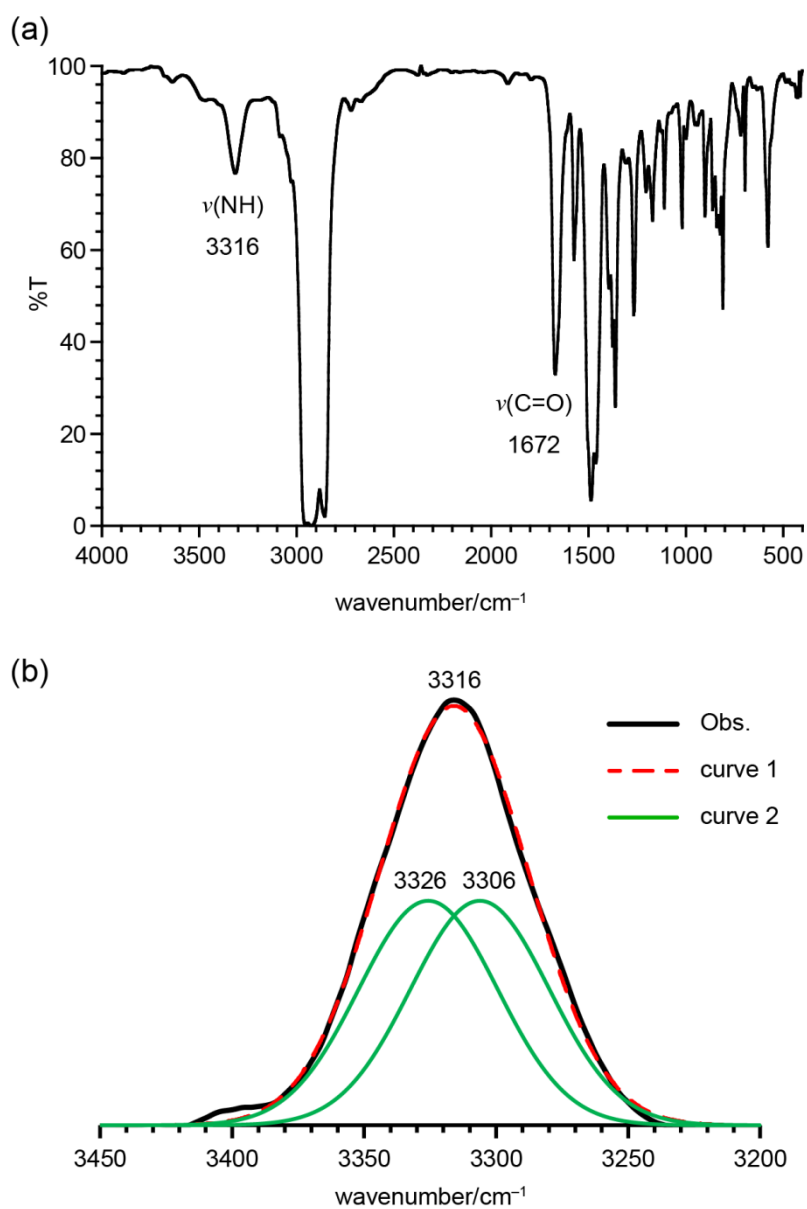
Fig. S4 (a) IR spectrum of the dioxotungsten complex **2-W** in the solid state (Nujol method) and (b) Curve-fitting data at the region around v(NH) bands by Gaussian distribution using a open sourse software fityk 0.9.8.[4] Curve 1 (red, dashed) represents the single Gaussian curve fitting, and curve 2 (green, solid) represents two Gaussian curves.
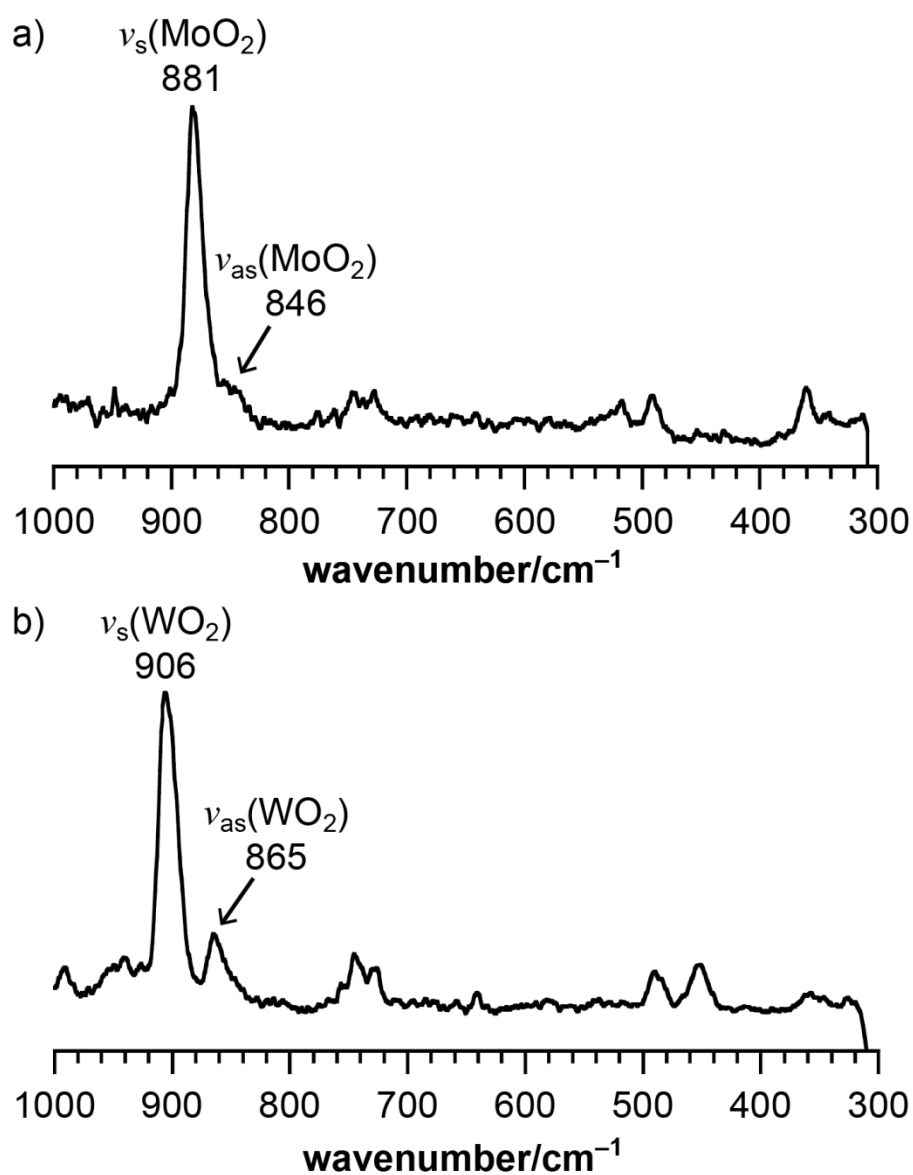
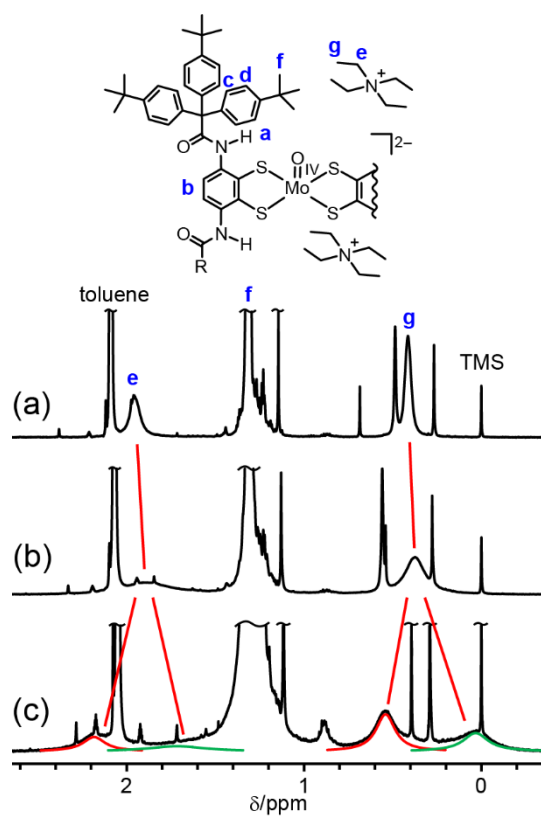**Fig. S5** Resonance Raman spectra of (a) **2-Mo** and (b) **2-W** excited at 514.5 nm in the solid state.

Fig. S6 VT NMR spectra and fitted curves using Lorentzian distribution[4] (green and red lines) of the monooxomolybdenum complex **1-Mo** in toluene-d_8 at (a) 303 K, (b) 263 K, and (c) 228 K.
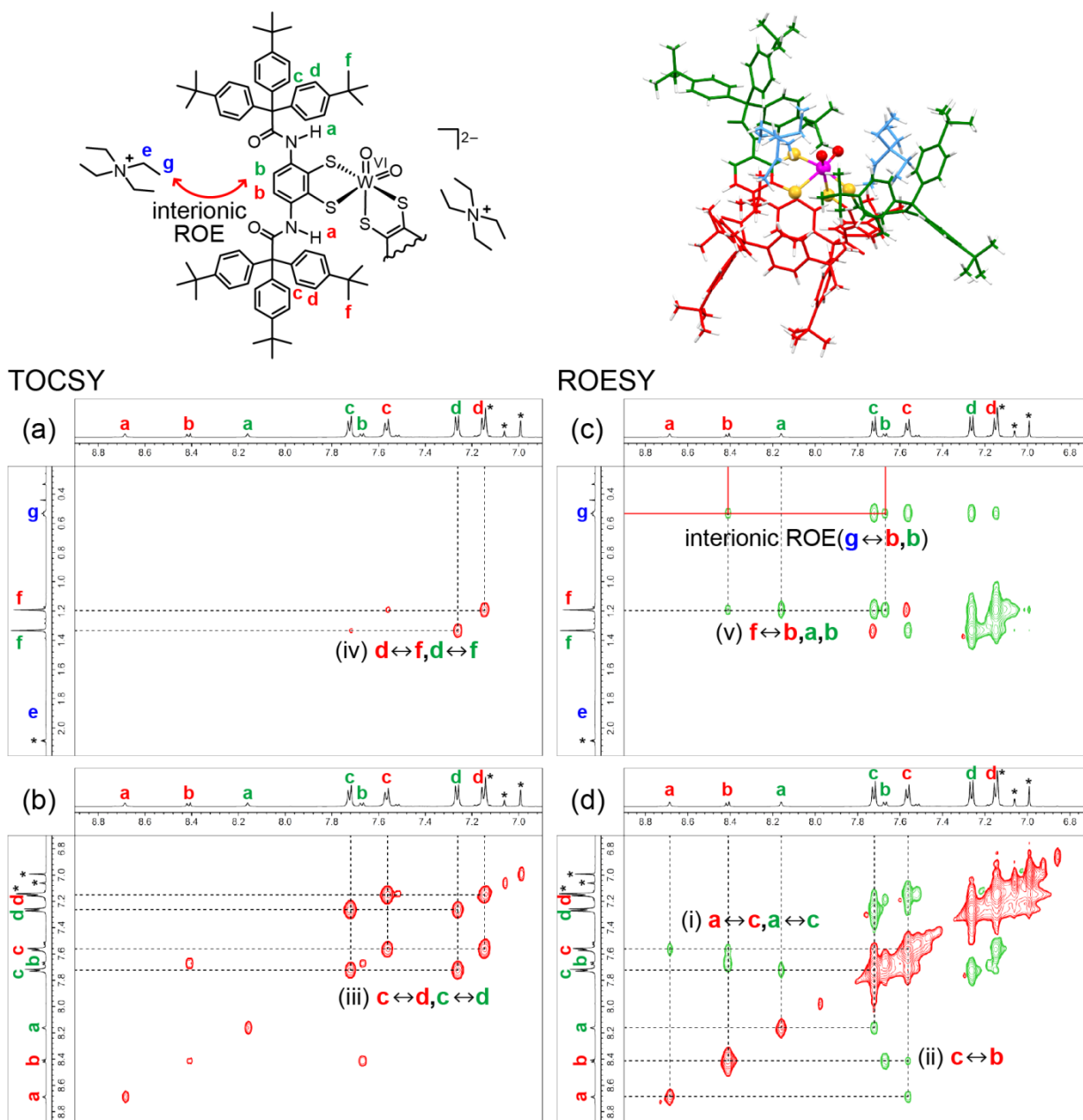
Fig. S7 (a,b) TOCSY and (c,d) ROESY spectra of **2-W** in toluene-d_8 at 228 K. The asterisks denote the residual signals of toluene-d_8. Assignment of red and green protons is represented in (i) to (v).

References

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