

Electronic Supporting Information

Structurally Characterized One Oxo-Desoxo Bridged Mo₂-bis(dithiolene) Complex and its Interconversion to Discrete Oxo or Desoxo DMSOR Model

*Golam Moula, Moumita Bose and Sabyasachi Sarkar**

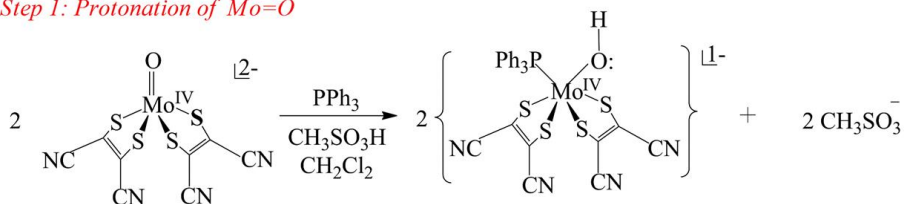
*Nanoscience and Synthetic Leaf Laboratory at Downing Hall, Center for Healthcare Science and
Technology, Indian Institute of Engineering Science and Technology, Shibpur, Botanic Garden,
Howrah 711103, West Bengal, India.*

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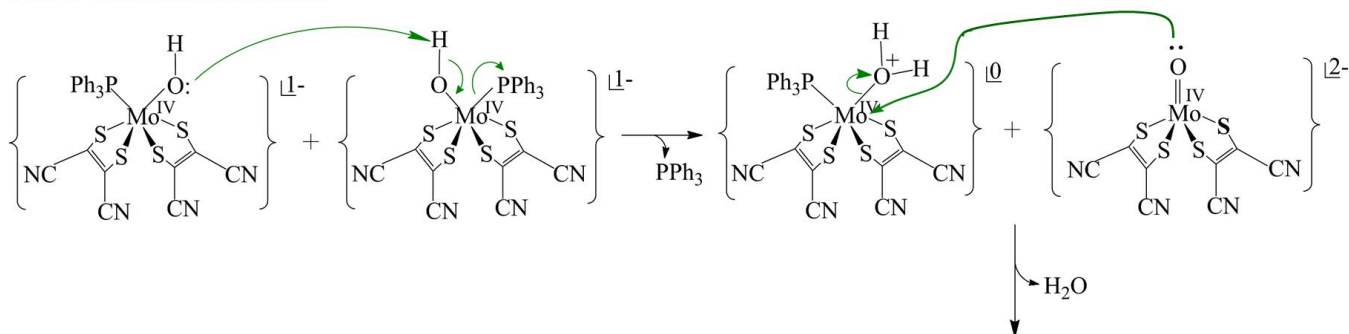
1. Tentative Mechanisms for the Formation of the Complexes 1, 2 and 3

Step 1: Protonation of Mo=O

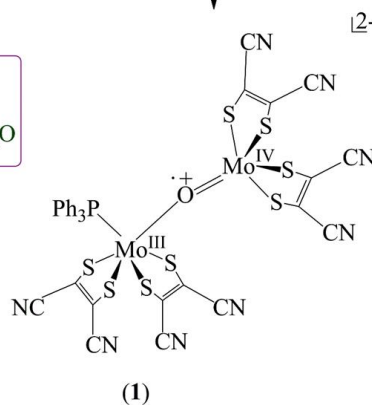
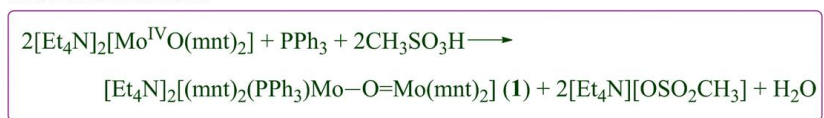


Step 2: Condensation reaction and Product (1) formation

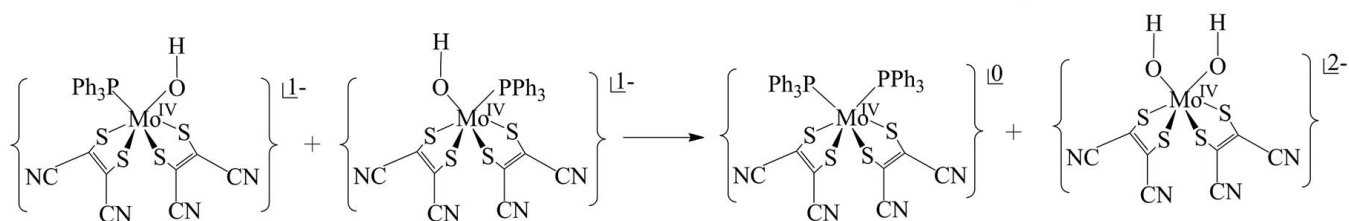
Path 1: Condensation reaction :



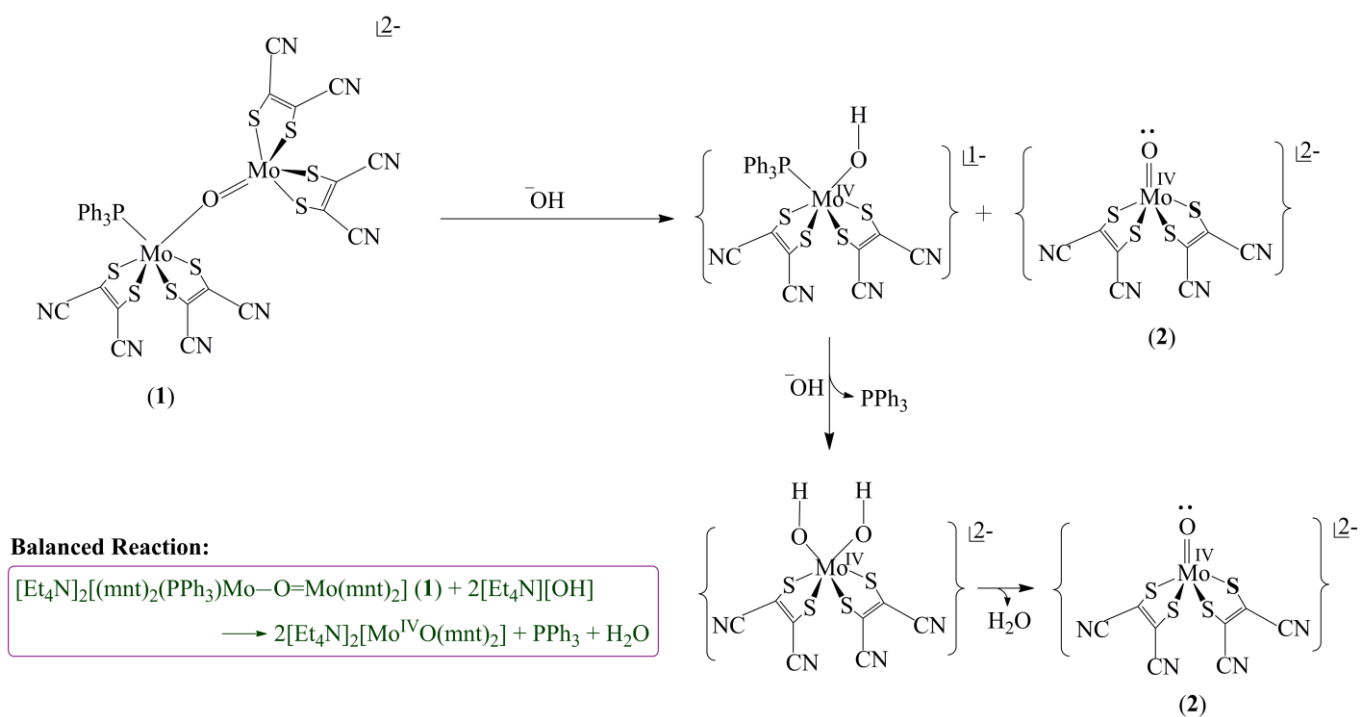
Balanced Reaction:



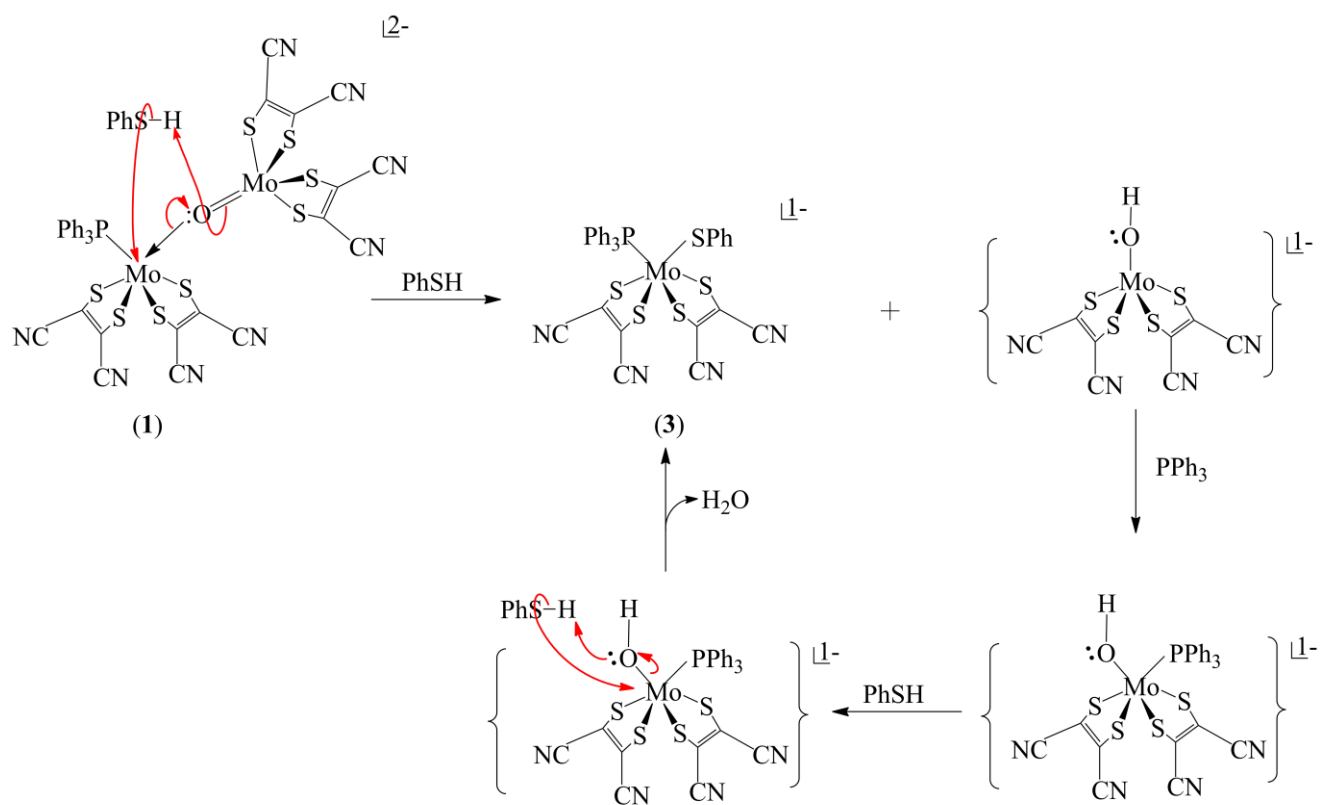
Path 2: Inter ligand exchange :



Scheme S1. A tentative mechanism for the formation of the complex (1).



Scheme S2. A tentative mechanism for the formation of the complex (2).



Scheme S3. A tentative mechanism for the formation of the complex (3).

2. Conversion of the Complex 1 into Tris:

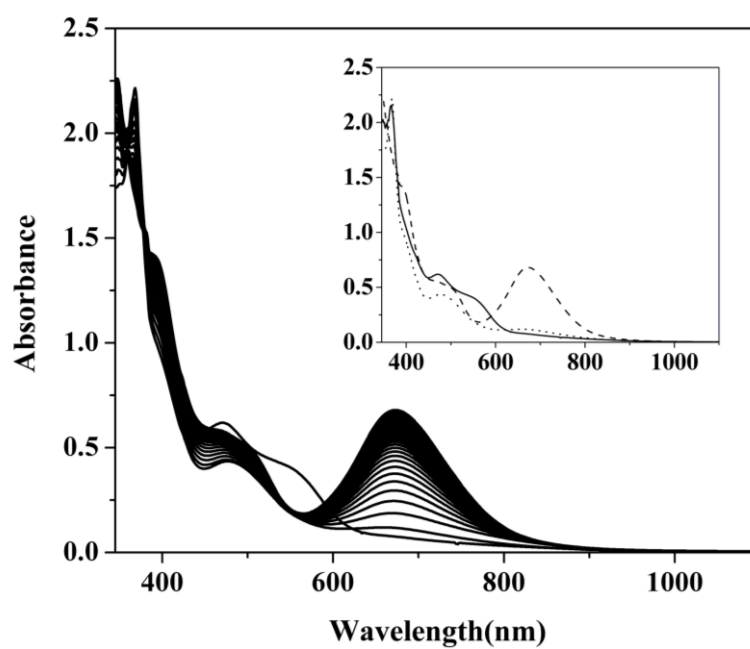


Figure S-1. Conversion of $[\text{Et}_4\text{N}]_2[\text{Mo}(\text{PPh}_3)(\text{mnt})_2\text{-O-Mo}(\text{mnt})_2]$ (**1**) to $[\text{Et}_4\text{N}]_2[\text{Mo}^{\text{IV}}(\text{mnt})_3]$ in dichloromethane at 25°C. Concentration of $[\text{Et}_4\text{N}]_2[\text{Mo}(\text{PPh}_3)(\text{mnt})_2\text{-O-Mo}(\text{mnt})_2]$ (**1**) = 1×10^{-4} M. Total time = 16 min. Scan rate = 15 Sec / scan. Inset: immediate spectra of complex (solid line), after 15 seconds (dotted line) and final tris (dithiolene) species(dashed line).

3. UV-Vis of the Raw Reaction Soup and Isolated Complex 1:

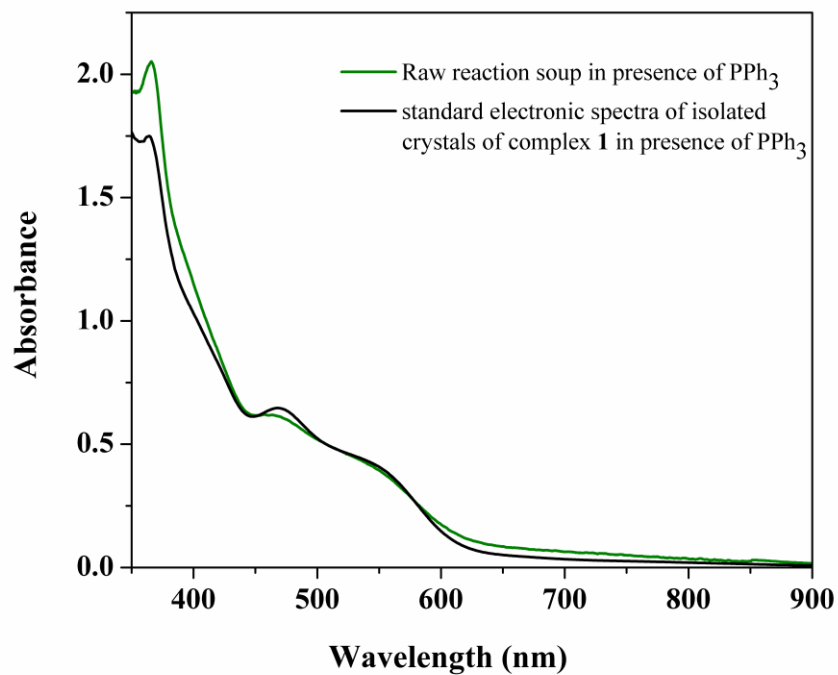


Figure S-2. UV-Vis absorption spectra of raw reaction soup (green) from which complex **1** was isolated and isolated complex **1** (10^{-4} M). Both in presence of excess PPh₃ (black) in dichloromethane.

4. Mo–O=Mo Plane is Bisecting the Molecule:

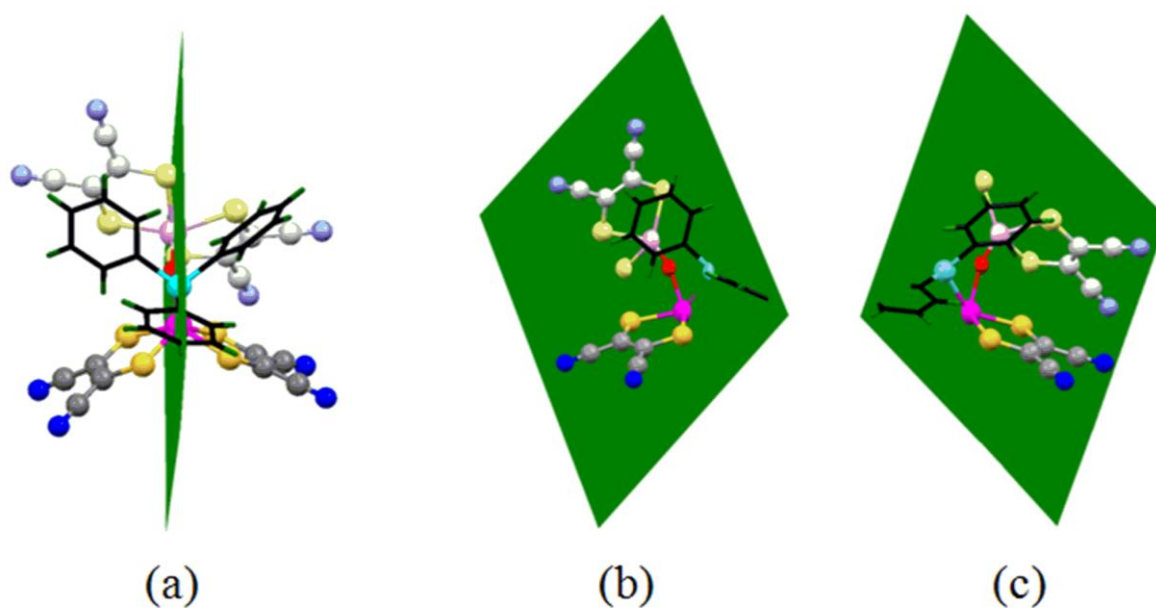


Figure S-3. Plane containing Mo–O=Mo is bisecting the molecule. (a) front view, (b) left-side view, (c) right-side view.

5. Structure of the Anion of the Complex 1 with Selected distances:

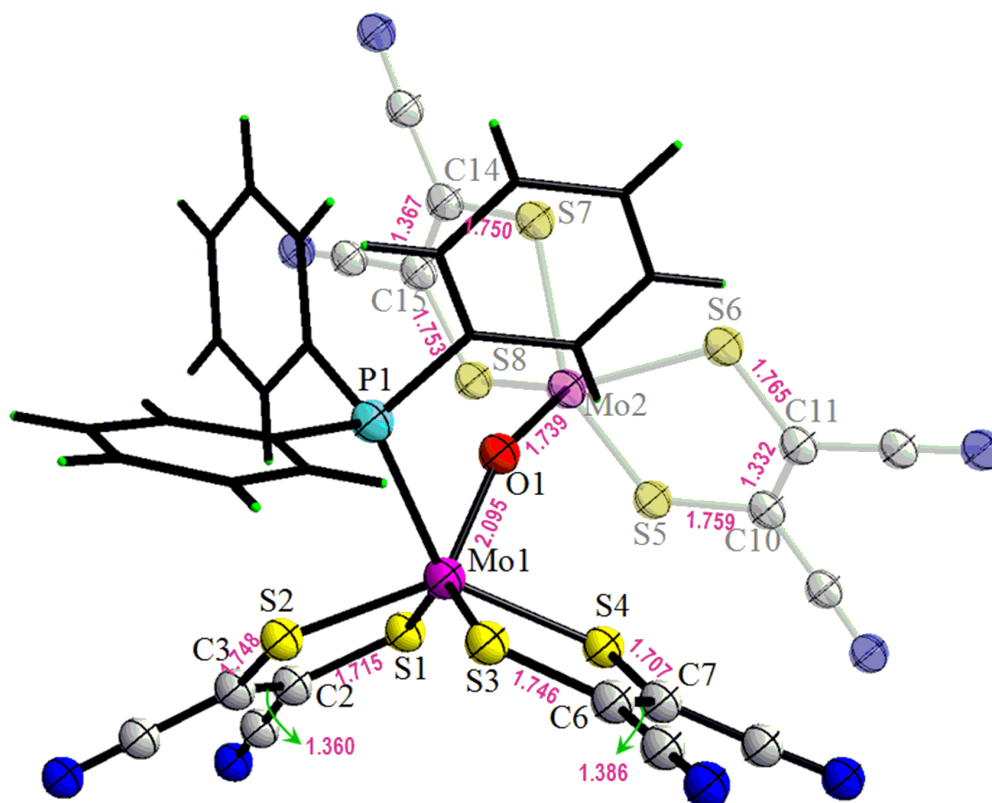


Figure S-4. Structure of the anion of **1** with selected distances and selected atoms labeling scheme. Five coordinated molybdenum with two mnt^{2-} has been lightened in colour for clarity.

6. Table S-1: Bond Valence Sum Calculations for complex 1

Mo	Assumed oxidation state	Bond valence sum	% Deviation from assumed oxidation state
1	+3	2.823	5.9
	+4	3.576	10.6
2	+3	3.567	18.9
	+4	4.38	9.5

7. Crystal Packing:

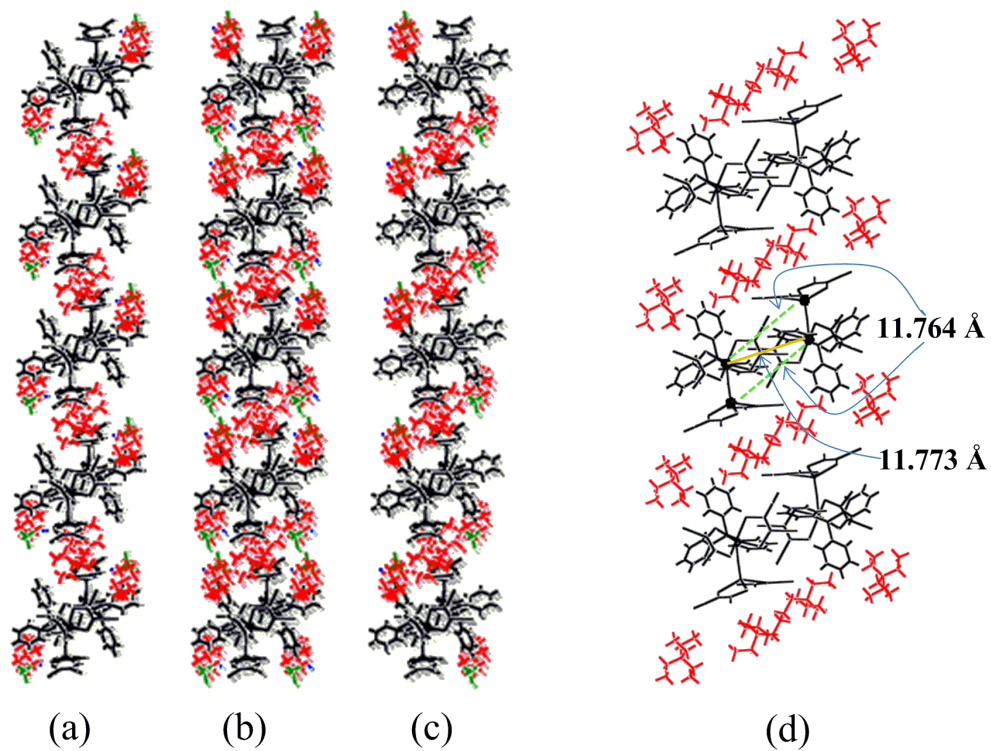


Figure S-5. Packing diagram. Anions are in black, dichloromethane in green and cations in red. Lattice water molecules are omitted for clarity. (a) right strand, (b) left and right strand together, (c) left strand of the complex **1**, (d) sandwiched anions by cations.

8. IR:

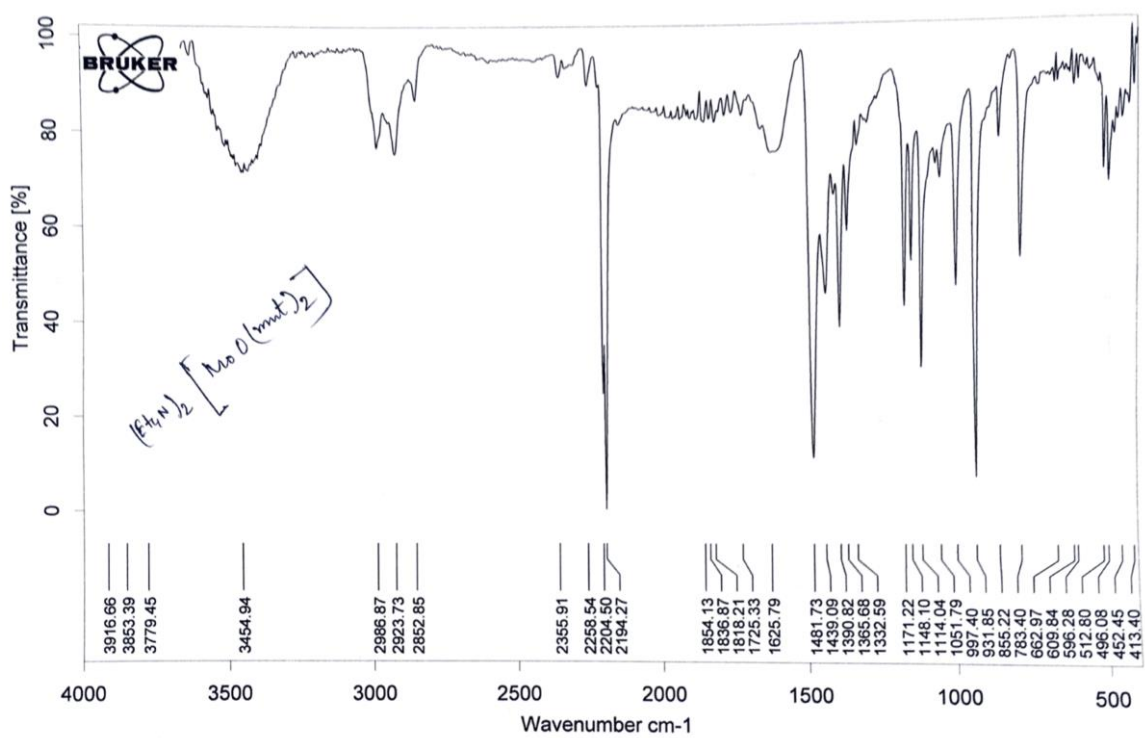
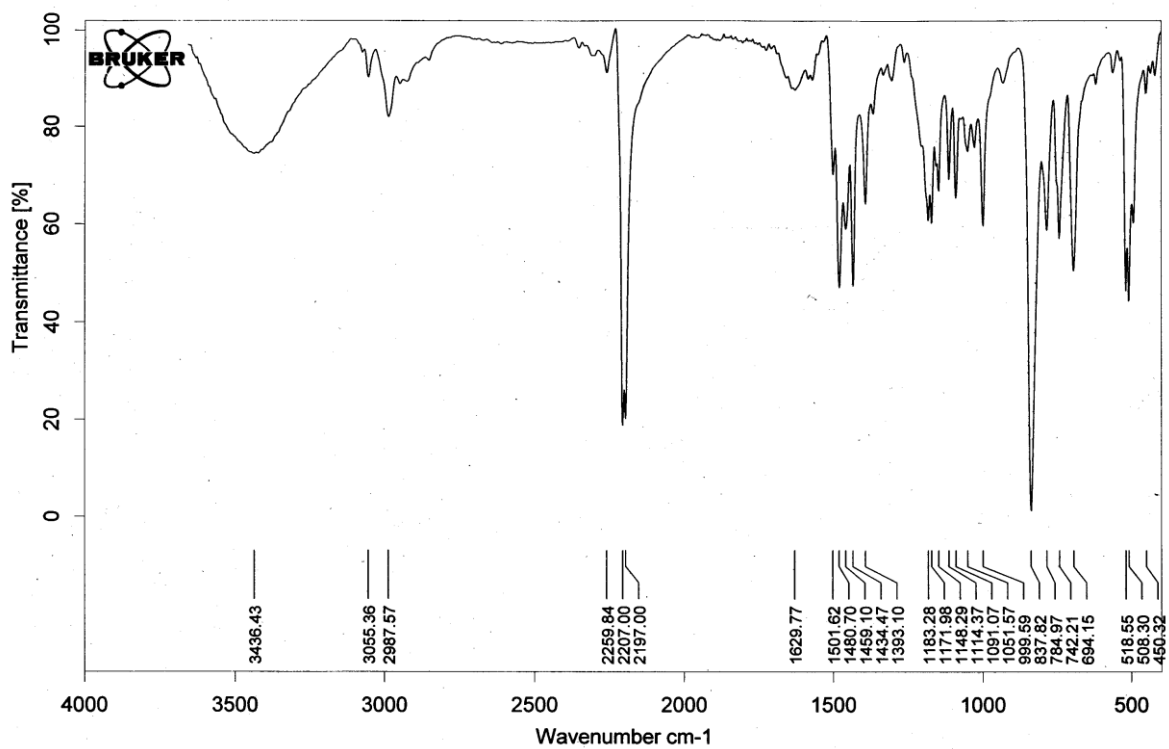


Figure S-6. IR (KBr pellet) spectra of the complex 1 (above) and the complex 2 (below).

9. EPR:

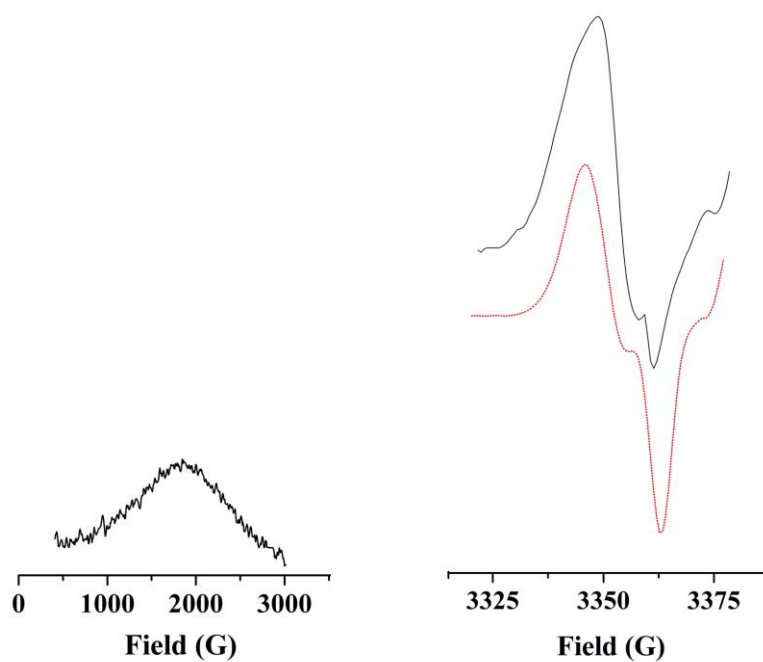


Figure S-7. Left: Broad EPR for $\Delta M_s = 2$. Right: Coupling due to ^{31}P ($I=1/2$, 100%, $a(^{31}\text{P})=8$ G). Black (experimental), Red (simulated).

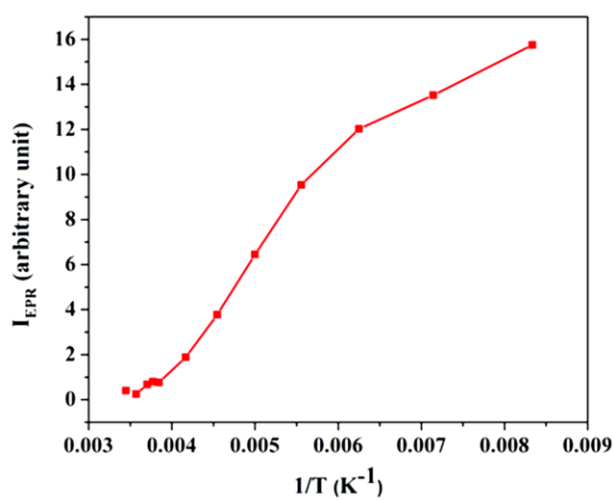


Figure S-8. EPR intensity (accomplished by double integration) as a function of $1/T$.

10. Magnetism.

The presence of the triplet state in **1** as envisaged from the EPR signal is further corroborated by the magnetic study (μ_{eff} , 1.41 B.M.). The unusual linear increase of $\chi_M T$ vs. T (Figure S-6) over a wide range from 10-300K demonstrates temperature independent paramagnetism (TIP).^[S1] Such magnetic behavior is consistent with the complex involving zero-field splitting superimposed with the exchange coupling between the ground singlet and excited triplet state resulting in TIP. A satisfactory fit on $\chi_M T$ vs. T curve (Figure S-6) was obtained using

$$\hat{H} = -2J\hat{S}_1\hat{S}_2 + D\left[\hat{S}_z^2 - \frac{1}{3}S(S+1)\right] + g\beta H\hat{S}_z + E(\hat{S}_x^2 - \hat{S}_y^2) \quad (1)$$

the spin Hamiltonian parameter, equation (1),^[S1-S3] where $-2J$ is the exchange coupling constant which turns out to be equal to the energy difference between the singlet-triplet states, all other terms have their usual meaning. Using $g = 1.971$ (fixed), $D = -83 \times 10^{-4} \text{ cm}^{-1}$ (fixed) and $E = 55 \times 10^{-5} \text{ cm}^{-1}$ (fixed) obtained from EPR, the best-fit parameters are $J = -0.50484 \text{ cm}^{-1}$ ($-144 \times 10^{-5} \text{ Kcal/mole}$), $\chi_{TIP} = 92 \times 10^{-5} \text{ cm}^3 \text{ mol}^{-1}$. Singlet state is lower in energy as is evident from the sign of the J value.^[S3] With such a small energy gap ($2J = -288 \times 10^{-5} \text{ Kcal/mole}$) there has been a detectable population in the triplet state under thermal equilibrium with the singlet state essentially in the entire temperature range.

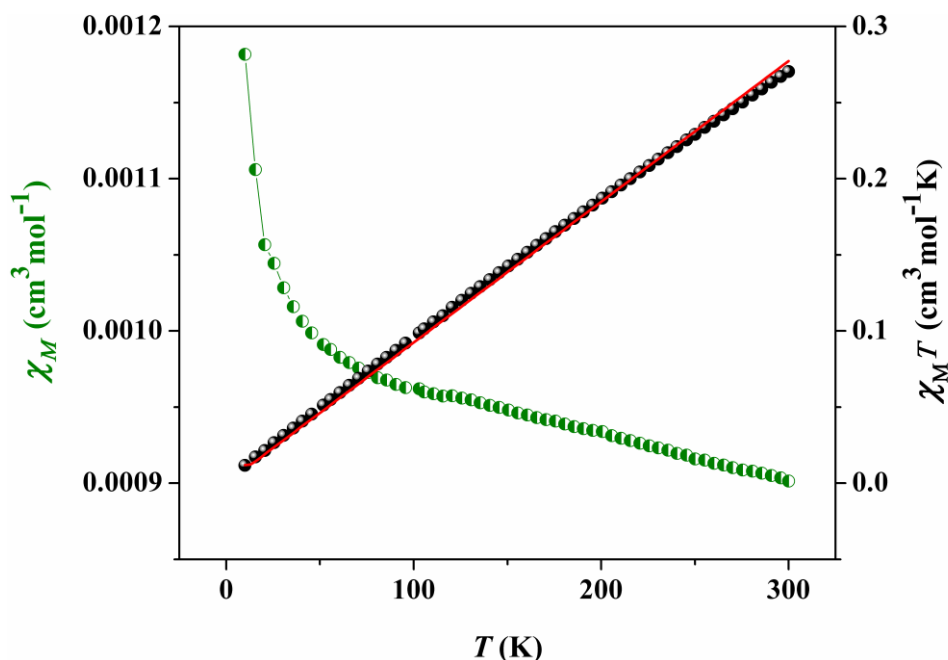


Figure S-9. Temperature dependence of χ_M (green circles) and $\chi_M T$ (black circles) of **1**. The black line shows the best fit of $\chi_M T$.

11. PL Spectra of the Complex 1 at Different Excitation Wavelengths:

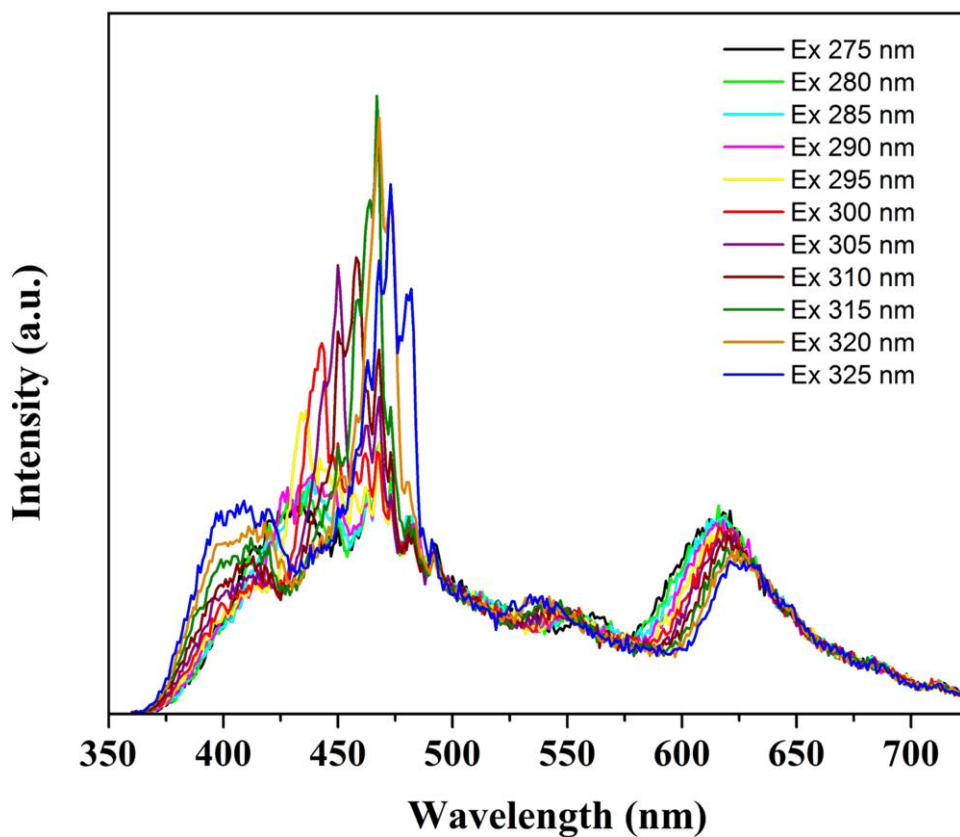


Figure S-10. Solid state room temperature luminescence spectra of complex **1** at different excitations from $\lambda_{\text{ex}} = 275$ nm to 325 nm at 5 nm intervals in air.

Table S-2. Emission maxima (λ_{em}), and lifetimes of the emitting species (τ) of complex **1** for excitation 325 nm.

λ_{em} (nm)	τ (μs)
470	7.58
615	11.45

12. Excitation Spectra of the Complex 1 for Emission at 470 nm and 615 nm Wavelengths:

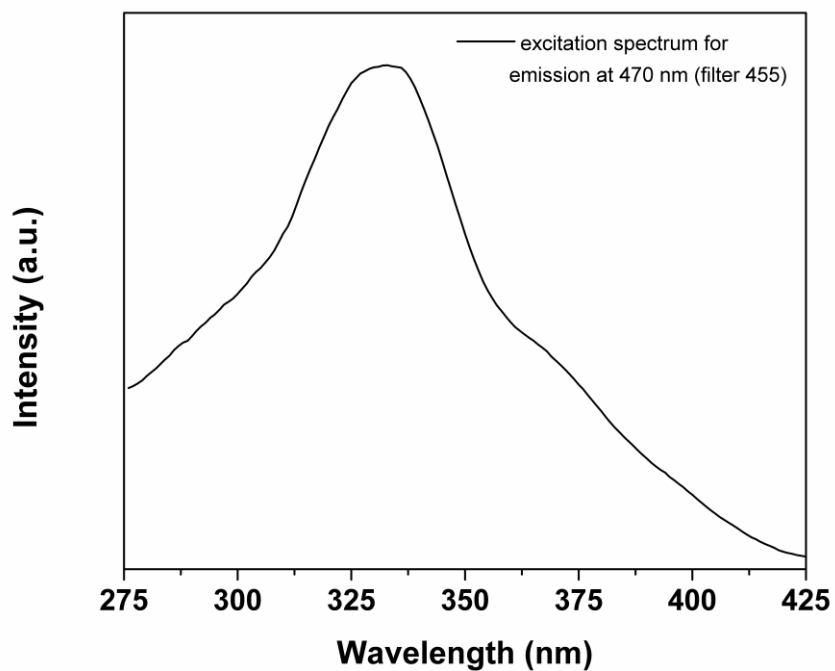


Figure S-11. Excitation spectrum of the complex 1 for emission at 470 nm wavelength.

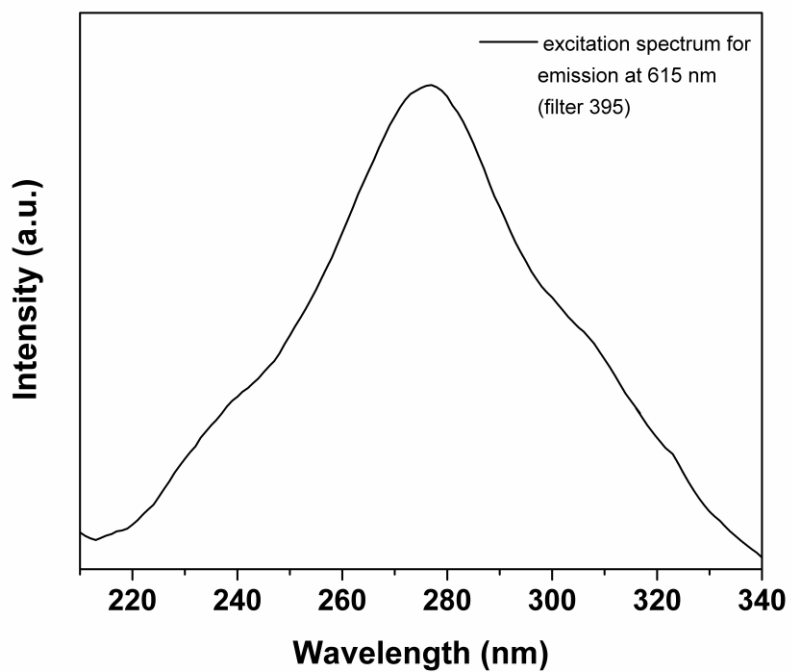


Figure S-12. Excitation spectrum of the complex 1 for emission at 615 nm wavelength.

13. Computational Details:

Table S-3. Optimized geometry of complex 1 in the singlet state in gas phase. $E = -5480.0435983$ (hartree).

Mo	1.11810800	-1.05505400	0.66649700
S	0.25377700	-0.92342500	2.90846600
S	3.14443900	-0.42571500	1.76594900
S	2.55548500	-2.44729000	-0.62946600
S	-0.32188100	-2.97742700	0.51179300
P	1.90741100	0.77195100	-1.04024200
O	-0.64174200	0.00613400	0.18704900
N	1.06945300	-0.47520600	6.52217100
N	4.87043600	0.28691500	4.98286100
N	3.12957700	-5.75067200	-2.22734400
N	-0.62273300	-6.54004000	-0.58529900
C	1.30223800	-0.50667300	5.38100300
C	1.57751900	-0.54906900	3.98032000
C	2.84103000	-0.31307900	3.48939700
C	3.94643200	0.01274400	4.32644800
C	2.50418500	-4.97634200	-1.61975000
C	1.77560300	-3.99589600	-0.88787400
C	0.52590400	-4.22622200	-0.36237400
C	-0.10926200	-5.49878600	-0.48962400
Mo	-2.36835500	0.48842500	0.07733900
S	-3.69285700	-0.85908200	1.56023700
S	-3.41367900	-0.84277700	-1.62667700
S	-2.64578800	2.27527400	-1.52916500
S	-2.79193800	2.23872800	1.67846200
C	-5.16334200	-3.13501000	1.25821600
C	-4.40701800	-2.14177500	0.57011800
C	-4.28508200	-2.14080400	-0.79295800
C	-4.90247500	-3.12570000	-1.61621300
C	-2.62009200	4.99246500	-1.33124200
C	-2.66087100	3.77502100	-0.59239100
C	-2.71979200	3.76079900	0.77619000
C	-2.73259000	4.96561400	1.53582700
N	-5.78471300	-3.92600300	1.84830800
N	-5.40019700	-3.90606200	-2.32615400
N	-2.72542400	5.93845600	2.18045000
N	-2.57245600	5.97049900	-1.96627600
C	3.73531800	0.93901700	-1.29812700
C	4.42283200	0.03645200	-2.12717600
H	3.87799400	-0.73604100	-2.65819700
C	5.80709500	0.12480900	-2.27897200
H	6.32005300	-0.58417200	-2.92379700
C	6.52767300	1.11078800	-1.60281200
H	7.60691800	1.17596600	-1.71860600
C	5.85494400	2.00850200	-0.77301700
H	6.40576000	2.77747500	-0.23734700
C	4.47020400	1.92357500	-0.62013300
H	3.96088800	2.62631500	0.03044300
C	1.40227500	2.47320500	-0.53225600
C	1.24552600	2.76021100	0.83208500
H	1.35245100	1.97182600	1.56884800
C	0.93040800	4.05443700	1.24945700
H	0.79304400	4.25696400	2.30762400
C	0.75401600	5.07124000	0.31083100
H	0.47434100	6.06929300	0.63605100
C	0.89354100	4.79021100	-1.05005500
H	0.71689400	5.56804100	-1.78735800
C	1.21486800	3.49982800	-1.47060700
H	1.29324900	3.29052800	-2.53180100
C	1.27190500	0.53078000	-2.75639100
C	1.89375900	1.13594400	-3.86297800
H	2.78503200	1.73992700	-3.72464600
C	1.38408000	0.95322100	-5.14874200
H	1.87660400	1.42819700	-5.99394400
C	0.24959100	0.16335100	-5.34771100
H	-0.14802500	0.02280700	-6.34980500
C	-0.37079600	-0.44516400	-4.25660900
H	-1.25748700	-1.05708300	-4.39233300
C	0.13814200	-0.26682500	-2.96865600
H	-0.35972000	-0.74296300	-2.13302500

Table S-4. Optimized geometry of complex 1 in the triplet state in gas phase. E = -5480.0346163(hartree).

Mo	0.91484600	-1.19463500	0.39341100
S	0.78769000	-0.30996500	2.71615800
S	3.21825400	-1.69695100	1.05831400
S	1.14472100	-2.43744600	-1.70031400
S	-0.10342300	-3.22563700	1.18392600
P	2.01403700	0.89859500	-1.05554100
O	-0.74259900	-0.07374700	0.15427100
N	2.42089800	-0.48272500	6.05352500
N	5.48587600	-2.18904000	3.94106600
N	0.99984200	-5.81918400	-3.20561400
N	-0.67360400	-6.81616400	0.43093900
C	2.34570800	-0.67230200	4.90603900
C	2.23615900	-0.88871900	3.49694700
C	3.27430700	-1.46730300	2.79659500
C	4.48384400	-1.86109800	3.44271200
C	0.82702700	-5.04684800	-2.34958600
C	0.64516500	-4.07237700	-1.32318800
C	0.09212700	-4.39723200	-0.10445000
C	-0.33169000	-5.73085200	0.17940100
Mo	-2.42539300	0.61404800	0.23492100
S	-3.83202400	-0.78128500	1.57119900
S	-3.68131300	-0.31947700	-1.58483800
S	-2.57694500	2.63118500	-1.06134500
S	-2.55418600	2.12590900	2.09582800
C	-5.55746800	-2.82240300	1.02951600
C	-4.72086700	-1.82479100	0.44957600
C	-4.65333600	-1.63233500	-0.90321800
C	-5.40692200	-2.41509500	-1.82461600
C	-2.28435500	5.27661200	-0.48063200
C	-2.39195400	3.97125000	0.07786500
C	-2.37337200	3.75268100	1.43006600
C	-2.23831200	4.82556300	2.35862400
N	-6.24147400	-3.62199800	1.53193800
N	-6.01203300	-3.03167400	-2.60811400
N	-2.12504900	5.68988700	3.13355500
N	-2.18961000	6.33067600	-0.97260900
C	3.83075900	0.77990000	-1.39881600
C	4.30632100	-0.35689100	-2.07501200
H	3.61604700	-1.14073900	-2.37298800
C	5.66335800	-0.49500600	-2.36120700
H	6.01272700	-1.38336800	-2.88081300
C	6.56934400	0.49400600	-1.96989400
H	7.62907800	0.38091500	-2.18557700
C	6.10740400	1.62213800	-1.29272000
H	6.80445300	2.39555300	-0.97924900
C	4.74637100	1.76659100	-1.00930200
H	4.40075000	2.64830500	-0.48065000
C	1.82312900	2.53172600	-0.22561800
C	2.20138000	2.64064900	1.12364000
H	2.57921000	1.77332600	1.65446600
C	2.06807900	3.85445800	1.79713400
H	2.35018800	3.91902100	2.84436800
C	1.54290100	4.96862000	1.13848100
H	1.41057800	5.90548800	1.67261300
C	1.15903100	4.86695600	-0.19939700
H	0.71939700	5.71954500	-0.70826800
C	1.29723000	3.65478500	-0.87987400
H	0.97543800	3.58204100	-1.91274900
C	1.32364200	1.12925100	-2.75364500
C	2.06544500	1.76569000	-3.76452300
H	3.06864300	2.12509100	-3.55695100
C	1.52422500	1.93409700	-5.03865400
H	2.10981800	2.42772100	-5.81067900
C	0.23781200	1.46720600	-5.32180200
H	-0.18199400	1.59630300	-6.31642800
C	-0.50497600	0.83454800	-4.32567100
H	-1.50617500	0.46705200	-4.53039100
C	0.03316500	0.66462500	-3.04774400
H	-0.55730100	0.17109400	-2.28550100

Orbital energies from single point calculation by taking xyz of optimized singlet and triplet

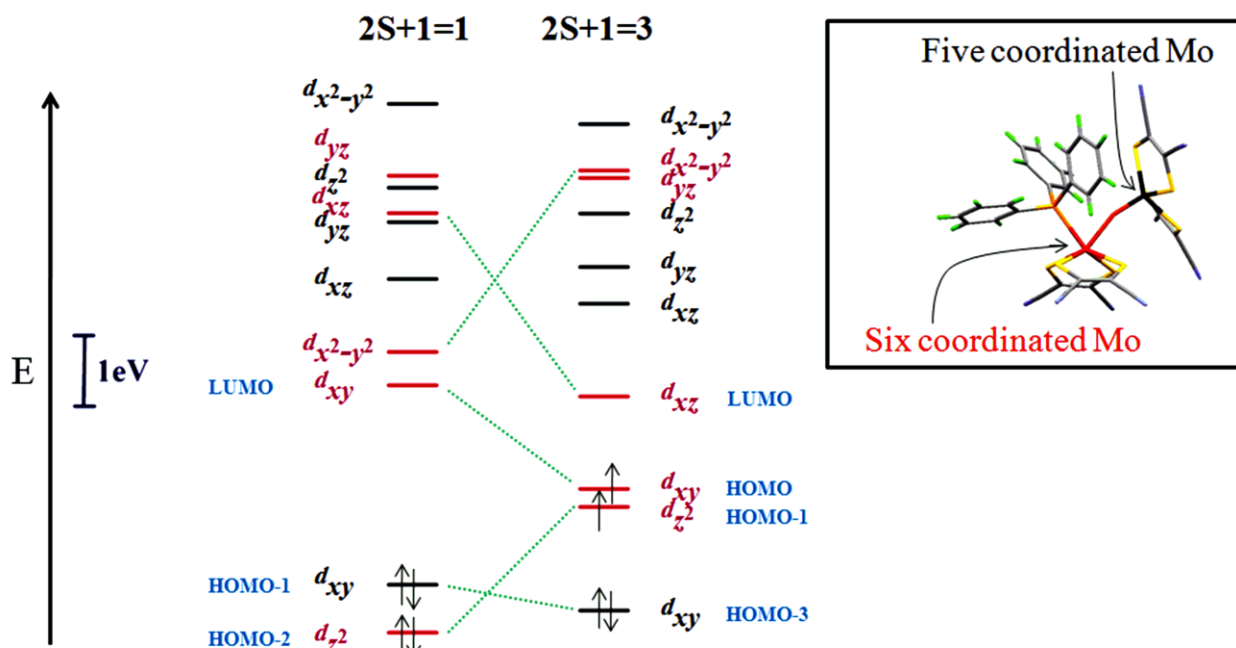


Figure S-13. Orbitals' energy in the singlet and triplet states. Red bars correspond to hexa-coordinated Mo and black bars correspond to penta-coordinated Mo.

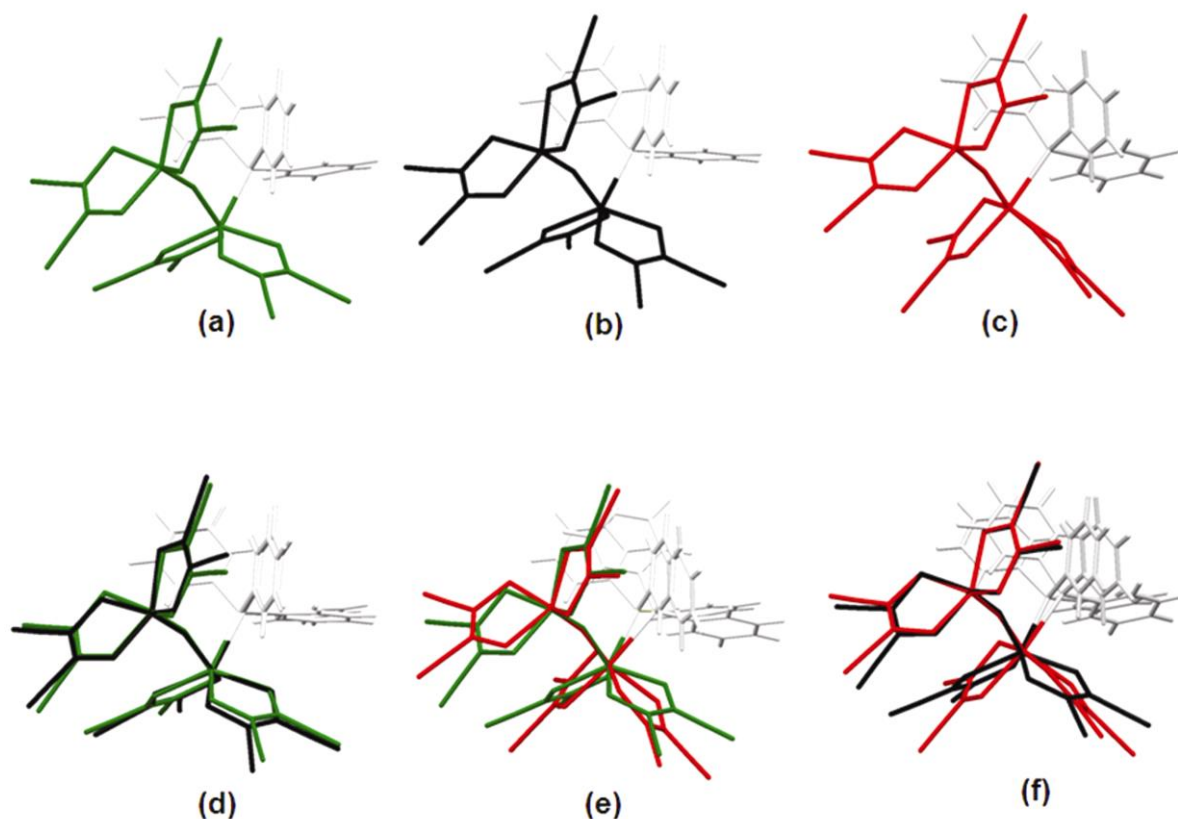


Figure S-14. Geometry of (a) X-ray structure, (b) optimized singlet, (c) optimized triplet, (d) Overlapping X-ray structure with optimized singlet, (e) Overlapping X-ray structure with optimized triplet (f), Overlapping optimized singlet with optimized triplet. Triphenylphosphine has shown as white for clarity.

Table S-5. Comparison of selected parameters obtained from crystal structure and DFT optimized structures

Parameters	Crystal Structure	Optimized Singlet	Optimized Triplet
Distances (Å)			
Mo(1) - S(1)	2.357(2)	2.406	2.489
Mo(1) - S(2)	2.320(2)	2.390	2.450
Mo(1) - S(3)	2.321(2)	2.384	2.446
Mo(1) - S(4)	2.374(2)	2.407	2.406
C(2) - S(1)	1.715(6)	1.744	1.744
C(3) - S(2)	1.749(6)	1.754	1.754
C(2) - C(3)	1.360(9)	1.376	1.379
C(6) - S(3)	1.746(6)	1.753	1.751
C(7) - S(4)	1.705(7)	1.744	1.752
C(6) - C(7)	1.388(9)	1.375	1.377
Mo(2) - S(5)	2.345(2)	2.402	2.390
Mo(2) - S(6)	2.361(2)	2.402	2.400
Mo(2) - S(7)	2.367(2)	2.419	2.403
Mo(2) - S(8)	2.348(2)	2.410	2.401
C(10) - S(5)	1.757(7)	1.771	1.771
C(11)-S(6)	1.764(7)	1.772	1.770
C(10) - C(11)	1.334(10)	1.369	1.368
C(14) - S(7)	1.749(6)	1.768	1.769
C(15) - S(8)	1.753(6)	1.771	1.768
C(14) - C(15)	1.368(9)	1.370	1.370
Mo(2) - O(1)	1.739(4)	1.796	1.820
Mo(1) - O(1)	2.094(4)	2.110	2.015
Mo(1) - P(1)	2.542(2)	2.622	2.773
Angles (°)			
Mo(2)-O(1)-Mo(1)	159.1(2)	161.92	164.93
O(1)-Mo(1)-P(1)	74.06(11)	75.68	81.03
Mo(1)-S-C _{dithiolene} ^a	108.35	108.59	105.49
Mo(2)-S-C _{dithiolene} ^a	105.15	106.32	106.46

^aaverage

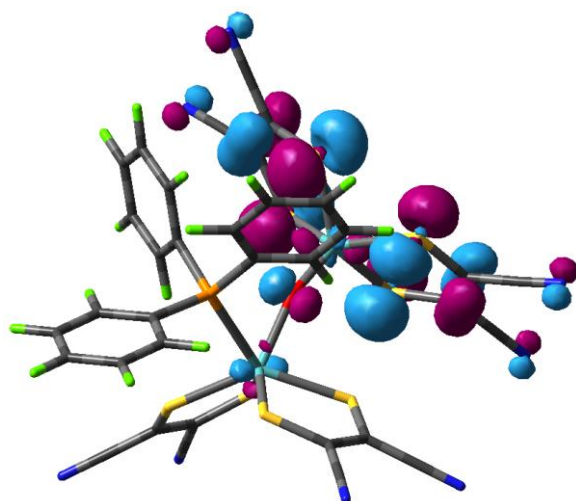


Figure S-15. HOMO for the complex **1** in the ground singlet state.

Table S-6. TD-DFT calculations based on the ground state geometry.

State	Energy (eV)	Main excitation(%) ^[a]	Assignment (f) ^[b]	TD-DFT λ_{\max} (nm) ^[c]	Exp. λ_{\max} (nm)
3	1.7569	H-2→L(31) H-1→L(19) H→L(42)	M'MLCT ML'MLCT (0.0254)	705	657
8	2.3073	H-4→L(28) H-3→L(52)	L'MLCT (0.0248)	537	553
13	2.6463	H-4→L+1(38) H-3→L(52)	L'MLCT (0.0233)	468	470
25	3.1544	H-6→L(50) H-2→L+3(10)	L'MLCT (0.045)	393	395
40	3.5193	H-3→L+4(42) H-2→L+4(11)	LLCT (0.0299)	352	362
41	3.5218	H-9→L(15) H-4→L+3(20) H-3→L+3(45)	LLCT (0.0203)	352	
69	4.0040	H-13→L(11) H- 5→L+4(15) H- 4→L+5(11)	LLCT (0.0332)	309	294
102	4.4061	H-13→L+1(11) H-9→L+2(42)	LLCT (0.0714)	281	

^[a] H and L denote HOMO and LUMO, respectively. ^[b] The values between parentheses indicate oscillator strength, f. ^[c] In gas phase.

14. References:

- S1. M. M. Rohmer, I. P. C. Liu, J.-C. Lin, M. J. Chiu, C.-H. Lee, G.-H. Lee, M. Benard, X. Lopez, S.-M. Peng, *Angew. Chem. Int. Ed.* 2007, **46**, 3533-3536.
- S2. R. Boca, *Coord. Chem. Rev.* 2004, **248**, 757-815.
- S3. O. Kahn, *Molecular Magnetism*; VCH: New York, 1993.