Supporting Information

for

Study of asymmetrical mixed-valent Mo_2–Mo_2 complexes in the class III regime

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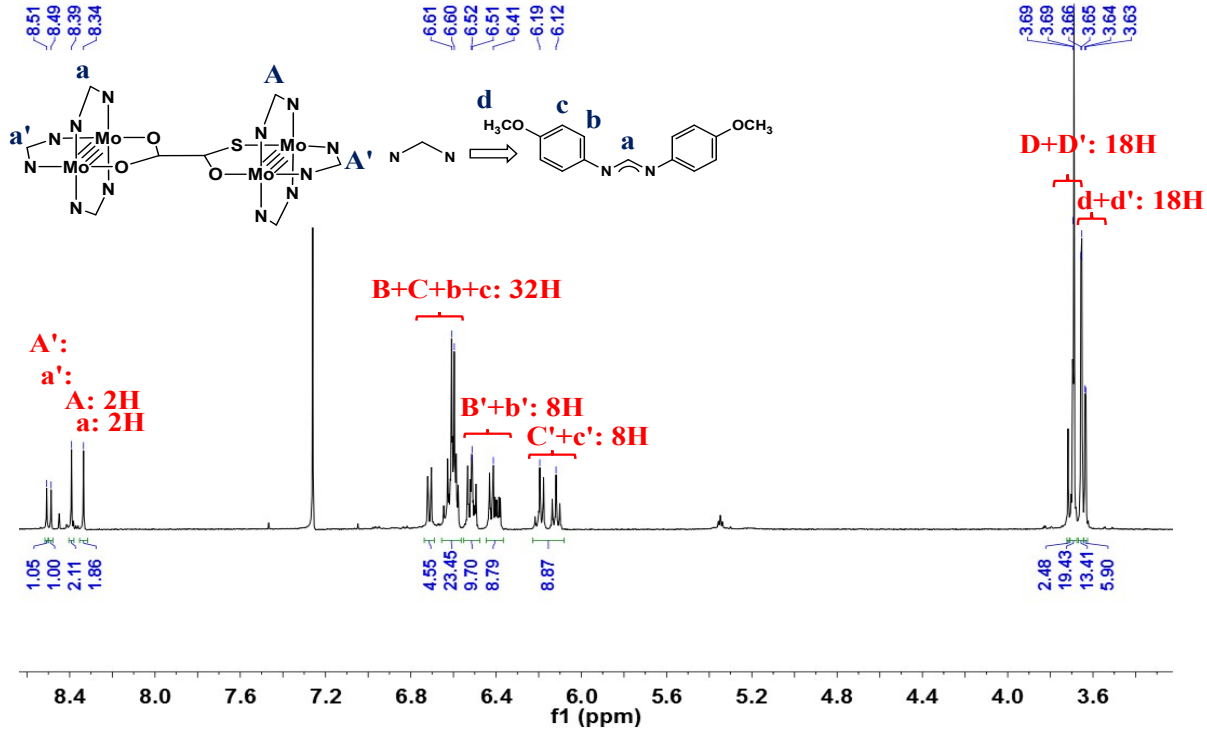

Fig.S1 ^{1}H NMR spectrum of compound [**OO–OS**].

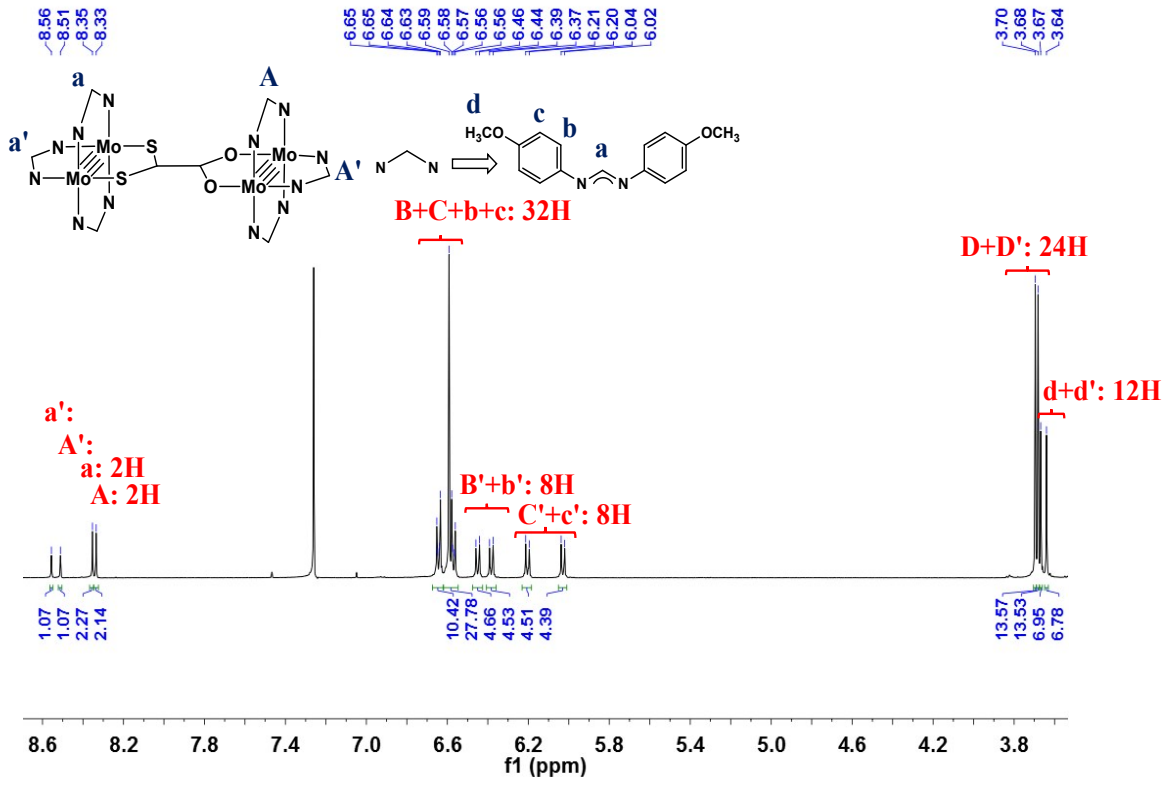

Fig.S2 ^{1}H NMR spectrum of compound [**SS–OO**].

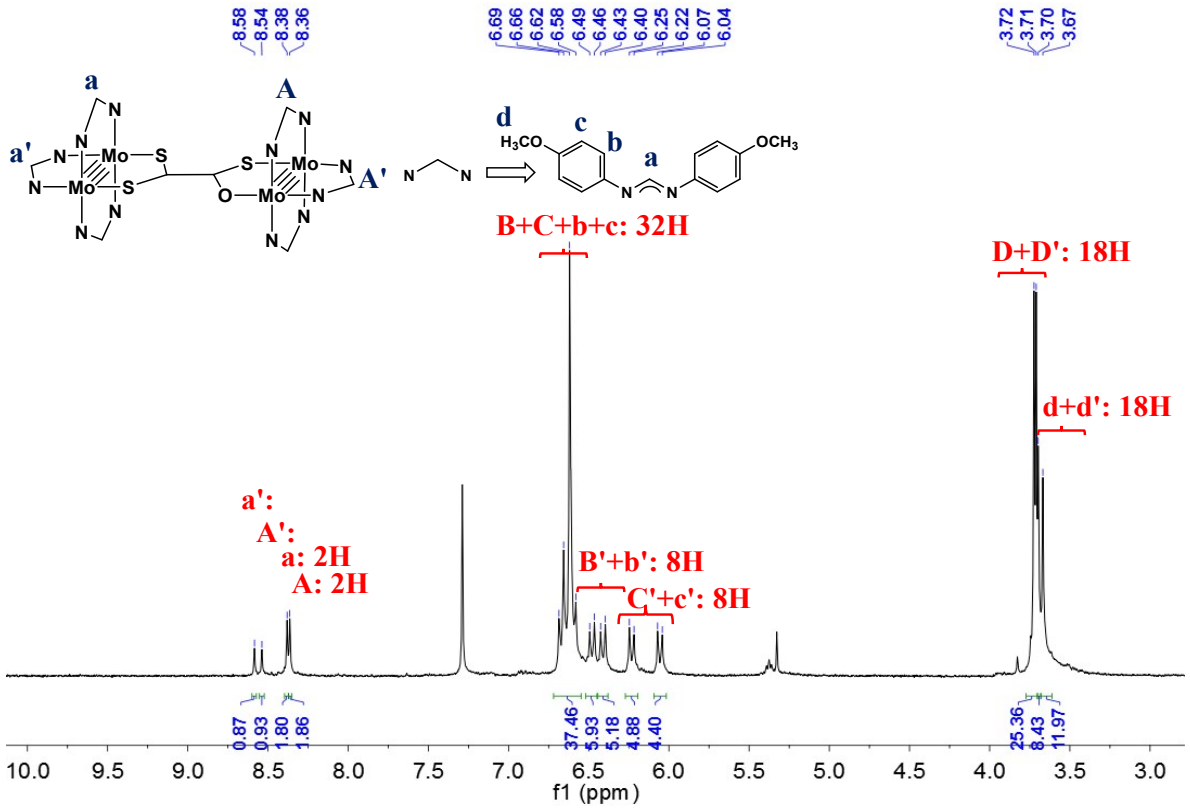

Fig.S3 ^{1}H NMR spectrum of compound [**SS–OS**].

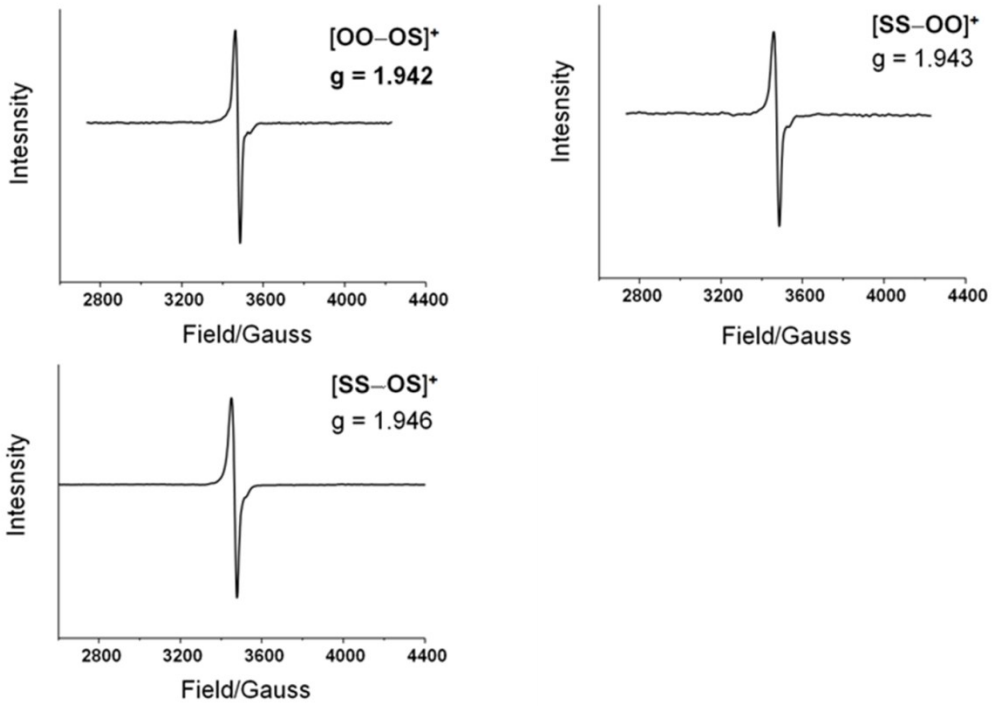

Fig. S4 X-band EPR spectra of the asymmetric MV cations generated by single electron oxidation of the neutral compounds. Samples were measured in CH_2Cl_2 solutions at 173 K.

Tables:

Table S1 Crystallographic data and collection parameters for [**SS–OO**]·4CH_2Cl_2 and [**SS–OS**]·4CH_2Cl_2.

Compound	[**SS–OO**]·4CH_2Cl_2	[**SS–OS**]·4CH_2Cl_2
Formula	$C_{96}H_{98}N_{12}O_{14}S_2Cl_8Mo_4$	$C_{96}H_{98}N_{12}O_{13}S_3Cl_8Mo_4$
Fw	2375.34	2391.40
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$
a (Å)	12.4057(6)	12.4214(5)
b (Å)	14.4700(6)	14.4786(7)
c (Å)	15.4898(7)	15.4651(7)
α (deg)	72.209(4)	72.182(4)
β (deg)	83.612(4)	83.891(4)
γ (deg)	71.215(4)	71.230(4)
V (Å^3)	2506.3(2)	2507.0(2)
Z	1	1
T (K)	173	173
R_1[a]	0.0520	0.0819
wR_2[b]	0.1458	0.2324
GOF on F^2	1.054	1.067

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR_2 = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$

Table S2 Spectroscopic data of the neutral asymmetric complexes in comparison with the symmetric analogues.

Complex	E_{MLCT}(cm^{-1})	ε_{MLCT}($M^{-1}cm^{-1}$)
[**OO–OS**]	17240	17985
[**SS–OO**]	14730	14502
[**SS–OS**]	13700	45893
[**OO–OO**]	21740	13025
[**OS–OS**]	14640	22275
[**SS–SS**]	11240	38025

Table S3 Selected DFT optimized bond lengths of [**OO–OS**]', [**SS–OO**]', [**SS–OS**]'.

Bond length (Å)	[**OO–OS**]'		[**SS–OO**]'		[**SS–OS**]'	
	OO	OS	OO	SS	OS	SS
Mo(1)─Mo(2)	2.154	2.158	2.153	2.160	2.159	2.161
Mo(1)─N(1)	2.129	2.141	2.132	2.162	2.152	2.161
Mo(1)─N(3)	2.130	2.151	2.131	2.163	2.141	2.162
Mo(1)─N(5)	2.144	2.149	2.145	2.151	2.150	2.150
Mo(2)─N(2)	2.144	2.144	2.144	2.151	2.144	2.150
Mo(1)─O(1)	2.129	─	2.126	─	2.078	─
Mo(2)─O(2)	2.133	2.086	2.124	─	─	─
Mo(1)─S(1)	─	2.489	─	2.456	2.484	2.454
Mo(2)─S(2)	─	─	─	2.454	─	2.455
C(1)─C(2)	1.498		1.486		1.474	

Table S4 Fragment composition (%) of the frontier molecular orbitals for the MV computational models ([**OO–OS**]')$^+$, ([**SS–OO**]')$^+$ and ([**SS–OS**]')$^+$.

	([**OO–OS**]')$^+$				([**SS–OO**]')$^+$				([**SS–OS**]')$^+$			
Orbital	Mo_2	COS	Mo_2	COO	Mo_2	COO	Mo_2	CSS	Mo_2	COS	Mo_2	CSS
HOMO−1	21.2	6.8	42.5	12.1	45.1	15.7	16.1	7.9	35.5	16.2	30.0	11.2
SOMO	49.2	4.4	26.3	2.6	20.8	1.9	55.9	3.1	37.4	4.5	38.5	4.8
LUMO	4.8	28.1	10.5	46.8	13.1	48.2	5.2	18.2	12.4	34.5	9.8	26.5

Table S5 Cartesian coordinates (Å) for DFT energy-minimized model compounds of [**OO–OS**]'.

Atoms	x	y	z
Mo	-0.639285	1.988224	3.344599
Mo	-1.620646	0.083369	3.089346
H	-1.406141	3.087237	5.918397
C	-0.062851	0.357409	0.529411
N	-2.274933	3.035144	2.424195
N	-3.306365	0.999197	2.129515
N	-1.524977	2.291565	5.280923
N	-2.567490	0.259302	5.001005
N	1.067106	1.064691	4.272459
N	0.030136	-0.966756	3.966822
C	-3.301046	2.323081	1.957540
H	-4.134466	2.822666	1.424644
C	-2.337484	1.341683	5.746338
H	-2.816343	1.447863	6.739289
C	1.085859	-0.263434	4.383936
H	1.970708	-0.778943	4.807260
H	-2.338377	4.038737	2.218558
H	0.373315	2.087044	-4.455611
H	0.142850	-1.982490	4.063710
H	3.940061	-3.010583	-1.386523
H	1.879678	-3.953995	-1.833772
H	2.322968	-2.245658	-6.830501
H	0.741351	-3.412159	-5.613848
H	-4.115743	0.528573	1.709077
O	-0.141451	-1.193402	-1.295900
O	1.259051	0.573545	-1.472925
C	0.379144	-0.111265	-0.822941
Mo	0.508173	-1.829578	-3.225564
Mo	1.847499	-0.150546	-3.386506
N	1.992832	-3.015273	-2.232796
N	3.423441	-1.219425	-2.402384
N	1.081299	-2.568150	-5.138678

N	2.515514	-0.775519	-5.310482
N	-1.119110	-0.705404	-4.051663
N	0.312880	1.088408	-4.225875
C	3.175719	-2.456518	-1.966426
H	1.929953	1.520696	4.589852
C	1.997931	-1.889827	-5.834497
C	-0.912422	0.577045	-4.361188
H	-1.748153	1.209737	-4.718902
S	0.514483	1.877527	1.142411
O	-0.870252	-0.385330	1.200348
H	4.343342	-0.859205	-2.124306
H	-2.094340	-1.005753	-4.162411
H	-3.202780	-0.419390	5.436535
H	3.211864	-0.319337	-5.911571

Table S6 Cartesian coordinates (Å) for DFT energy-minimized model compounds of [**SS–OO**]'.

Atoms	x	y	z
Mo	-0.762964	1.891941	3.380558
Mo	-1.959645	0.103706	3.443518
H	-2.017300	-1.228547	-4.451165
C	-0.408660	0.271631	0.928688
N	-2.309716	2.979622	2.368401
N	-3.589312	1.066901	2.437776
N	-1.466471	2.521051	5.291052
N	-2.747811	0.608780	5.359363
N	0.924194	0.887039	4.238141
N	-0.354935	-1.025530	4.307952
C	-3.431333	2.332507	2.044388
H	-4.219320	2.837534	1.451143
C	-2.347018	1.747329	5.931591
H	-2.738574	2.045415	6.922747
C	0.816313	-0.416475	4.505001
H	1.689715	-0.986284	4.878711
H	-2.260222	3.933856	1.994130
H	0.207905	2.053031	-4.572597
H	-4.465752	0.639457	2.117572
H	4.165875	-2.922207	-1.727015
H	1.866920	1.264593	4.387203
H	-1.217761	3.376025	5.802276
H	-3.426272	0.080307	5.920283
H	2.491825	-1.973963	-6.916629
H	4.371529	-0.683615	-2.258442
H	-0.338761	-2.030945	4.513785
H	0.980033	-3.308045	-5.792536
S	-0.479002	-1.583162	-1.112266
S	1.223517	0.925339	-1.197402
C	0.095374	-0.116122	-0.414722
Mo	0.568445	-1.846097	-3.316190
Mo	1.780123	-0.059114	-3.377313
N	2.172722	-2.986826	-2.449366
N	3.462145	-1.083675	-2.515027
N	1.245426	-2.462874	-5.274507
N	2.540043	-0.558794	-5.340110

N	-1.087211	-0.843858	-4.251287
N	0.202118	1.058924	-4.318473
C	3.329340	-2.372198	-2.201150
H	2.147759	-3.965801	-2.143109
C	2.118714	-1.685498	-5.914158
H	3.212943	-0.028382	-5.904908
C	-0.952114	0.442676	-4.572765
H	-1.794205	0.996252	-5.032687
O	0.003060	1.373955	1.466350
O	-1.252985	-0.500459	1.533696

Table S7 Cartesian coordinates (Å) for DFT energy-minimized model compounds of [**SS–OS**]'.

Atoms	x	y	z
Mo	-0.603714	1.931819	3.448082
Mo	-2.005071	0.294790	3.613265
H	-0.755086	3.501587	5.887728
C	-0.419951	0.062933	0.588581
N	-2.101905	3.218342	2.598089
N	-3.591370	1.474353	2.770332
N	-1.132794	2.677623	5.407153
N	-2.628258	0.934138	5.581278
N	0.962184	0.772442	4.359559
N	-0.529676	-0.968629	4.535780
C	-3.327640	2.729708	2.408139
H	-4.113693	3.354995	1.941647
C	-2.060332	2.020942	6.103523
H	-2.357761	2.375657	7.109972
C	0.696387	-0.481738	4.724950
H	1.489113	-1.116588	5.166633
H	-1.980009	4.179686	2.260589
H	-0.231607	1.963708	-4.260049
H	-0.635913	-1.951612	4.810512
H	4.121260	-2.804832	-1.680974
H	2.343697	-4.039380	-2.487918
H	2.779876	-1.395247	-6.981096
H	1.395670	-3.063841	-6.176837
H	-4.546157	1.169339	2.550878
S	-0.529861	-1.931161	-1.387416
O	0.814688	0.348984	-1.429016
C	0.013562	-0.395666	-0.743669
Mo	0.612970	-2.002222	-3.589871
Mo	1.567794	-0.084735	-3.316096
N	2.267107	-3.035166	-2.685763
N	3.268214	-0.987149	-2.368819
N	1.502926	-2.273343	-5.530864
N	2.515232	-0.227741	-5.231273
N	-1.106318	-1.095244	-4.508416
N	-0.100264	0.948653	-4.181208
C	3.281620	-2.312387	-2.210639
H	1.936817	1.053607	4.514327
C	2.300404	-1.306379	-5.986781
C	-1.146223	0.233698	-4.602424
H	-2.041286	0.740331	-5.014607
S	0.327709	1.490870	1.220257

S	-1.632207	-0.811161	1.454106
H	4.068051	-0.508393	-1.939493
H	-1.964531	-1.560641	-4.824613
H	-3.329660	0.494982	6.188231
H	3.139605	0.464564	-5.661067

Table S8 Cartesian coordinates (Å) for DFT energy-minimized model compounds of ([**OO–OS**]')$^{+}$.

Atoms	x	y	z
Mo	-0.719979	1.939104	3.372115
Mo	-1.740234	0.036088	3.121497
H	-1.455468	3.047318	5.942278
C	-0.185384	0.303598	0.570349
N	-2.352977	3.005844	2.482221
N	-3.413453	0.982940	2.185162
N	-1.591128	2.252214	5.307005
N	-2.666272	0.235171	5.029063
N	0.959167	0.987585	4.309511
N	-0.108924	-1.029173	3.998851
C	-3.398602	2.309910	2.038163
H	-4.244109	2.825948	1.544856
C	-2.415558	1.314862	5.771659
H	-2.889686	1.427838	6.764166
C	0.948366	-0.338321	4.433496
H	1.810554	-0.864471	4.885429
H	-2.419619	4.016719	2.314488
H	0.240051	2.028104	-4.447019
H	-0.027475	-2.044636	4.128294
H	3.873277	-3.014606	-1.380447
H	1.820174	-3.985613	-1.809628
H	2.241093	-2.255186	-6.749910
H	0.673570	-3.448687	-5.541264
H	-4.251138	0.528407	1.803322
O	-0.245599	-1.245078	-1.250743
O	1.122413	0.538295	-1.427933
C	0.255676	-0.158226	-0.776495
Mo	0.405392	-1.875541	-3.163000
Mo	1.730061	-0.162335	-3.322099
N	1.910279	-3.032508	-2.180396
N	3.314826	-1.213497	-2.348156
N	1.001005	-2.599151	-5.066342
N	2.408138	-0.781580	-5.236348
N	-1.221925	-0.779636	-4.008786
N	0.184065	1.037622	-4.182162
C	3.089592	-2.460471	-1.930595
H	1.815209	1.435033	4.657433
C	1.907727	-1.904256	-5.756771
C	-1.025906	0.498830	-4.338743
H	-1.860350	1.106608	-4.735848
S	0.419778	1.815789	1.180082
O	-1.003193	-0.436845	1.230538
H	4.241768	-0.849044	-2.098880
H	-2.184597	-1.106371	-4.152952
H	-3.311586	-0.434521	5.464679
H	3.098680	-0.312870	-5.835040

Table S9 Cartesian coordinates (Å) for DFT energy-minimized model compounds of ([**SS–OO**]')$^{+}$.

Atoms	x	y	z
Mo	-0.750147	1.894135	3.362416
Mo	-1.958280	0.090679	3.426771
H	-2.000149	-1.245014	-4.479031
C	-0.403195	0.266840	0.926081
N	-2.300026	2.974141	2.361168
N	-3.581598	1.059930	2.431701
N	-1.458464	2.518133	5.265075
N	-2.741936	0.603695	5.334557
N	0.920486	0.889301	4.235215
N	-0.361136	-1.024641	4.306165
C	-3.428094	2.330727	2.055913
H	-4.229009	2.845638	1.492436
C	-2.338325	1.742377	5.901951
H	-2.729348	2.040606	6.891389
C	0.802360	-0.408481	4.521358
H	1.663730	-0.969579	4.929755
H	-2.261803	3.939992	2.015272
H	0.226467	2.041668	-4.599146
H	-4.472564	0.640530	2.141044
H	4.179690	-2.932751	-1.787550
H	1.854109	1.276417	4.416278
H	-1.207888	3.373631	5.775187
H	-3.420094	0.073860	5.895196
H	2.472405	-1.958302	-6.887874
H	4.382756	-0.688787	-2.301227
H	-0.356930	-2.023479	4.543917
H	0.962789	-3.297655	-5.762351
S	-0.486451	-1.589610	-1.094195
S	1.225585	0.934862	-1.180135
C	0.097584	-0.118356	-0.409368
Mo	0.557758	-1.846564	-3.292787
Mo	1.776906	-0.047629	-3.354381
N	2.169527	-2.985515	-2.453933
N	3.459545	-1.080590	-2.520166
N	1.232956	-2.452645	-5.245999
N	2.526903	-0.547336	-5.311914
N	-1.082935	-0.848299	-4.244134
N	0.206959	1.056510	-4.311548
C	3.331787	-2.374140	-2.226524
H	2.156696	-3.976114	-2.184994
C	2.103212	-1.672705	-5.885123
H	3.197345	-0.011976	-5.875469
C	-0.939270	0.432850	-4.581883
H	-1.768819	0.976553	-5.072031
O	0.007531	1.371099	1.467936
O	-1.249930	-0.504606	1.535483

Table S10 Cartesian coordinates (Å) for DFT energy-minimized model compounds of ([**SS–OS**]')$^{+}$.

Atoms	x	y	z
Mo	-0.777615	2.121469	3.603165
Mo	-1.756061	0.195723	3.330193
H	-1.965091	-1.109438	-4.497964
C	-0.159394	0.490242	0.792007
N	-2.424132	3.156646	2.699564
N	-3.433592	1.111629	2.373335
N	-1.689071	2.411804	5.528286
N	-2.717541	0.372337	5.224713
N	0.898171	1.200620	4.578763
N	-0.121408	-0.836646	4.236566
C	-3.444283	2.439340	2.232381
H	-4.290559	2.938594	1.723543
C	-2.499933	1.454550	5.974744
H	-2.991688	1.552584	6.960258
C	0.913062	-0.125453	4.693200
H	1.779053	-0.636443	5.154904
H	-2.508226	4.166350	2.532472
H	0.468770	2.014044	-4.806777
H	-4.251112	0.640114	1.968973
H	4.156373	-3.100138	-1.885804
H	1.739694	1.663989	4.940962
H	-1.580174	3.205750	6.170224
H	-3.354874	-0.312274	5.648772
H	2.383572	-2.215842	-6.981987
H	4.492553	-0.896228	-2.492946
H	-0.017731	-1.851435	4.355325
H	0.821426	-3.407873	-5.767154
S	-0.386401	-1.429841	-1.138144
S	1.472401	0.977686	-1.383843
C	0.296810	0.040384	-0.525045
Mo	0.575932	-1.836602	-3.349346
Mo	1.910120	-0.125084	-3.514901
N	2.132291	-3.047129	-2.507215
N	3.541921	-1.235711	-2.679605
N	1.158856	-2.563000	-5.292217
N	2.573064	-0.751766	-5.466927
N	-1.016970	-0.767427	-4.303352
N	0.393498	1.042038	-4.485504
C	3.336945	-2.504937	-2.330178
H	2.061756	-4.023553	-2.198381
C	2.060753	-1.867866	-5.983062
H	3.260170	-0.283268	-6.068781
C	-0.798613	0.487497	-4.697228
H	-1.605097	1.066988	-5.184333
S	0.394864	2.028034	1.446044
O	-0.977984	-0.250057	1.461903