

Figure S1: Second derivative of the normalized S K-edge spectra of the dianionic (solid red line), monoanionic (dashed green line), and neutral (dotted blue line) Mo tris(dithiolene) complexes. The arrow denotes the feature corresponding to the S 1s \rightarrow 4p transition.

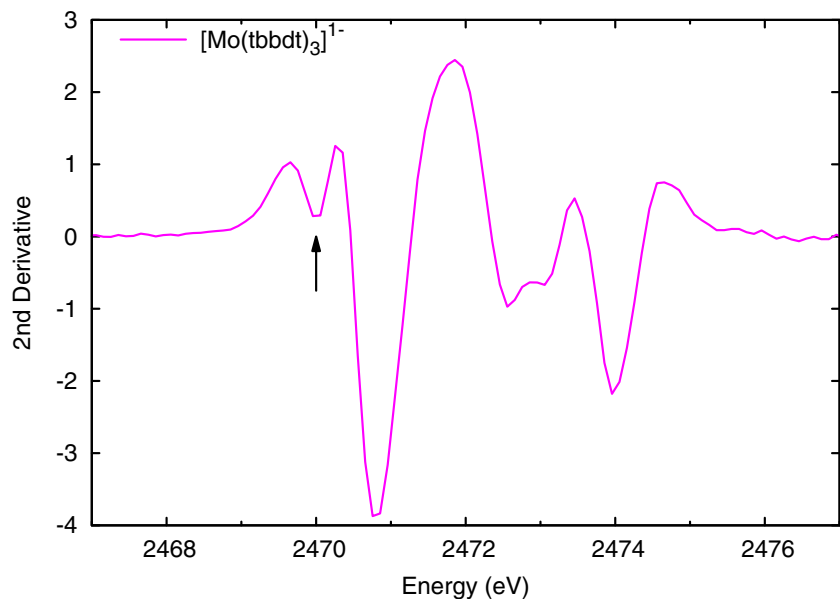


Figure S2: Second derivative of the normalized S K-edge spectrum of $[\text{Mo}(\text{tbbdt})_3]^{1-}$. The arrow denotes the feature corresponding to a transition to a predominately metal-based orbital.

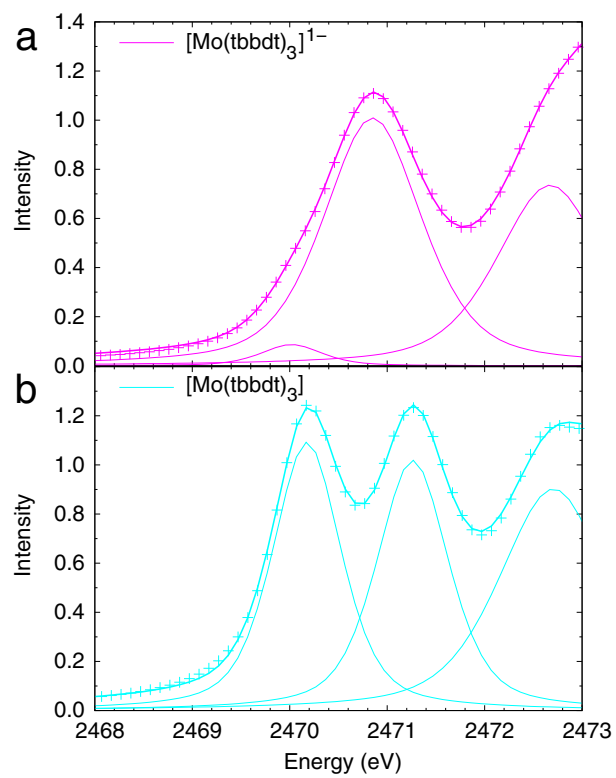


Figure S3: Representative fits of the [Mo(tbbdt)₃]^z (z = 1-, 0) complexes.

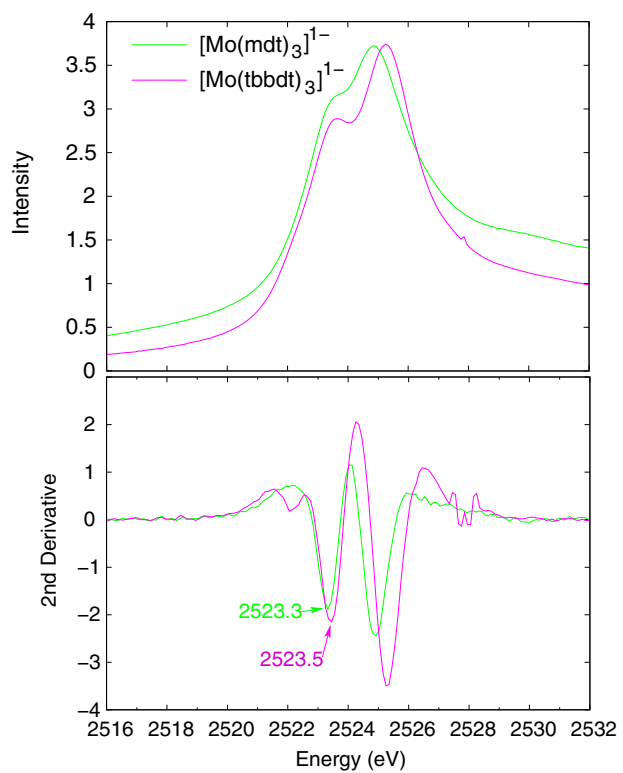


Figure S4: Normalized and second derivative Mo L₃-edge XAS data of $[\text{Mo}(\text{mdt})_3]^{1-}$ (green) and $[\text{Mo}(\text{tbbdt})_3]^{1-}$ (purple). The $[\text{Mo}(\text{tbbdt})_3]^{1-}$ data is from reference 16.

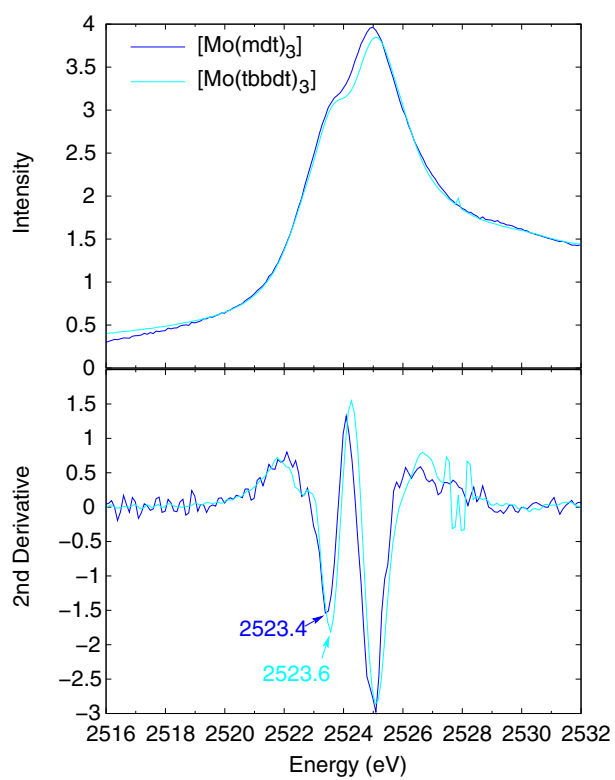


Figure S5: Normalized and second derivative Mo L₃-edge XAS data of [Mo(mdt)₃] (dark blue) and [Mo(tbbdt)₃] (light blue). The [Mo(tbbdt)₃] data is from reference 16.

The Cartesian coordinates of the geometry-optimized structures of $[\text{Mo}(\text{mdt})_3]^z$ ($z = 2-, 1-, 0$) and $[\text{Mo}(\text{bdt})_3]^z$ ($z = 1-, 0$). Geometry optimizations were performed in Gaussian 03 using the BP86 functional with the LanL2DZ basis set on Mo and the 6-311G* basis set on S, C, and H. $[\text{Mo}(\text{mdt})_3]^{2-}$ was optimized with two Et_4N^+ counterions, which have been removed below.

$[\text{Mo}(\text{mdt})_3]^{2-}$

Mo	0.00000	0.00000	0.00000
S	1.27550	1.34574	1.53415
S	1.23332	1.40841	-1.52199
C	2.29310	2.52955	-0.66636
C	2.31880	2.50957	0.69879
C	3.10537	3.43905	-1.56319
H	3.73689	4.13996	-0.98952
H	2.44597	4.03706	-2.22000
H	3.76865	2.85111	-2.22540
C	3.16131	3.38597	1.59683
H	3.76011	4.11221	1.02039
H	3.86573	2.78435	2.20566
H	2.53237	3.96201	2.30454
S	-1.79996	0.48918	-1.58688
S	-1.90469	0.31276	1.53415
C	-3.28036	0.97204	-0.71978
C	-3.33875	0.88762	0.64270
C	-4.35516	1.56126	-1.60999
H	-5.32875	1.65644	-1.09613
H	-4.50744	0.94898	-2.51947
H	-4.06044	2.56914	-1.96120
C	-4.49880	1.32237	1.51153
H	-5.41639	1.50943	0.92573
H	-4.26066	2.25536	2.06049
H	-4.73544	0.55680	2.27615
S	0.71255	-1.72983	-1.57835
S	0.43567	-1.88597	1.53415
C	1.30545	-3.16463	-0.70459
C	1.18100	-3.24605	0.65411
C	2.02222	-4.16990	-1.58263
H	2.20342	-5.13143	-1.06925
H	3.00318	-3.77262	-1.90802
H	1.45077	-4.37868	-2.50735
C	1.69931	-4.36688	1.52880
H	1.99156	-5.25683	0.94332
H	0.93789	-4.68314	2.26841
H	2.58820	-4.04517	2.10758

[Mo(mdt)₃]¹⁻

Mo	0.00000	0.00000	0.00000
S	-0.63082	1.73572	1.56692
S	-0.65748	1.72585	-1.56705
S	1.81822	-0.32333	1.56756
S	1.82359	-0.29487	-1.56707
S	-1.18831	-1.41402	1.56761
S	-1.16498	-1.43330	-1.56743
C	3.30986	-0.57212	0.68997
C	3.31228	-0.55923	-0.68900
C	4.57078	-0.79980	1.49901
C	4.57641	-0.77014	-1.49761
C	-1.15794	3.15314	0.68943
C	-1.17031	3.14860	-0.68956
C	-1.59445	4.35791	1.49832
C	-1.62148	4.34811	-1.49823
C	-2.15422	-2.57718	0.68955
C	-2.14318	-2.58630	-0.68953
C	-2.98295	-3.55481	1.49814
C	-2.95893	-3.57472	-1.49824
H	4.35647	-0.76996	2.58071
H	5.33812	-0.02904	1.28301
H	5.02864	-1.78356	1.27031
H	4.36311	-0.73708	-2.57941
H	5.04430	-1.75000	-1.27290
H	5.33539	0.00771	-1.27710
H	-1.49622	4.16357	2.57974
H	-2.65193	4.62320	1.29554
H	-0.98554	5.25248	1.25655
H	-1.54511	4.14600	-2.57999
H	-1.00677	5.24360	-1.27510
H	-2.67433	4.61624	-1.27610
H	-2.85939	-3.37694	2.57979
H	-2.69134	-4.60449	1.29098
H	-4.06239	-3.46710	1.26015
H	-2.80884	-3.41888	-2.57993
H	-4.04319	-3.47587	-1.28784
H	-2.67907	-4.62170	-1.26349

[Mo(mdt)₃]

Mo	0.00000	0.00000	0.00000
S	0.00528	1.82694	-1.56437
S	0.00664	1.82680	1.56437
S	-1.58268	-0.91310	-1.56434
S	-1.58284	-0.91257	1.56441
S	1.58268	-0.91310	-1.56434
S	1.58228	-0.91403	1.56417
C	-0.36406	3.27986	-0.69607
C	-0.36341	3.27982	0.69653
C	-0.63469	4.53081	-1.50377
H	-0.45774	4.35834	-2.57763
H	0.01068	5.36767	-1.17654
H	-1.68484	4.85898	-1.38161
C	-0.63291	4.53084	1.50452
H	-0.45826	4.35735	2.57858
H	-1.68208	4.86142	1.38058
H	0.01493	5.36650	1.17903
C	-2.65138	-1.96409	-0.69620
C	-2.65151	-1.96380	0.69650
C	-3.60580	-2.81777	-1.50292
H	-3.53978	-2.58387	-2.57767
H	-4.65253	-2.66423	-1.17902
H	-3.37740	-3.89337	-1.37512
C	-3.60593	-2.81727	1.50342
H	-3.54146	-2.58158	2.57788
H	-3.37605	-3.89280	1.37768
H	-4.65243	-2.66554	1.17799
C	3.03408	-1.28814	-0.69650
C	3.03388	-1.28863	0.69648
C	4.25936	-1.66118	-1.50291
H	4.02546	-1.72554	-2.57776
H	4.67146	-2.63567	-1.17946
H	5.05996	-0.90761	-1.37418
C	4.25892	-1.66217	1.50299
H	4.02407	-1.73002	2.57743
H	5.05845	-0.90691	1.37734
H	4.67291	-2.63501	1.17706

[Mo(bdt)₃]¹⁻

Mo	-0.01549	-0.03479	0.00545
S	0.90282	1.67647	1.46448
S	-0.42214	1.87843	-1.43540
C	0.74383	3.24024	0.66675
C	0.22057	3.31983	-0.64960
C	0.16439	4.57218	-1.29792
H	-0.23640	4.62270	-2.31558
C	0.60829	5.72900	-0.65183
H	0.55728	6.69387	-1.16787
C	1.11784	5.65146	0.65685
H	1.46461	6.55586	1.16844
C	1.18374	4.41740	1.30912
H	1.58091	4.34710	2.32703
S	1.75805	-0.68266	-1.51826
S	1.09584	-1.62806	1.46314
C	2.79509	-1.85223	-0.70394
C	2.54280	-2.21461	0.64466
C	3.42576	-3.09942	1.30055
H	3.22620	-3.36814	2.34303
C	4.53311	-3.62663	0.63149
H	5.20885	-4.31206	1.15438
C	4.77671	-3.27629	-0.70896
H	5.64262	-3.68830	-1.23844
C	3.91385	-2.39824	-1.36950
H	4.09715	-2.11766	-2.41185
S	-1.89191	-0.21523	1.53227
S	-1.52453	-1.21569	-1.48443
C	-3.21000	-1.03636	0.69853
C	-3.07171	-1.41303	-0.66287
C	-4.16463	-2.00501	-1.33218
H	-4.05008	-2.28554	-2.38432
C	-5.36987	-2.23367	-0.66400
H	-6.20824	-2.69519	-1.19693
C	-5.50298	-1.87146	0.68887
H	-6.44539	-2.05059	1.21772
C	-4.43177	-1.27983	1.36265
H	-4.52728	-0.99251	2.41485

[Mo(bdt)₃]

Mo	0.00000	0.00000	0.00000
S	1.17653	-1.38433	-1.58313
S	1.17657	-1.38428	1.58321
C	2.51592	-2.09297	-0.71434
C	3.57336	-2.73117	-1.41483
C	4.60437	-3.34482	-0.70856
C	2.51594	-2.09294	0.71442
C	4.60440	-3.34478	0.70862
C	3.57342	-2.73110	1.41490
H	3.56819	-2.72496	-2.51018
H	5.42312	-3.82791	-1.25280
H	5.42317	-3.82784	1.25286
H	3.56829	-2.72482	2.51025
S	0.61000	1.71031	-1.58298
S	0.60994	1.71032	1.58307
C	0.59912	3.22569	-0.71395
C	0.65509	4.45915	-1.41490
C	0.70553	5.65795	-0.70864
C	0.59908	3.22569	0.71403
C	0.70549	5.65796	0.70870
C	0.65500	4.45916	1.41497
H	0.74208	6.60792	1.25328
H	0.65223	4.45131	-2.51029
H	0.74216	6.60791	-1.25322
H	0.65208	4.45133	2.51036
S	-1.78609	-0.32730	-1.58246
S	-1.78606	-0.32739	1.58255
C	-3.10239	-1.07888	-0.71362
C	-4.20985	-1.62497	-1.41460
C	-5.28583	-2.15665	-0.70875
H	-4.20187	-1.62262	-2.51008
H	-6.13679	-2.57977	-1.25384
C	-3.10236	-1.07893	0.71370
C	-5.28580	-2.15671	0.70880
C	-4.20980	-1.62509	1.41466
H	-6.13674	-2.57989	1.25388
H	-4.20180	-1.62284	2.51014

Complete References

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