Supporting Information for

Tuning the electronic structure of MoMo quadruple bonds by N for O for S substitution

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Figure S1. Solid state structure of the second crystallographically independent core of **Mo₂NS**, with anisotropic displacement parameters drawn at the 50% level and hydrogen atoms omitted for clarity. Atoms with a prime ('), double prime (") and triple prime (") character are generated using the symmetry operations '1-x, -y, z', '-y+1/2, x-1/2, -z+1/2' and 'y+1/2, -z+1/2', respectively.



Figure S2. Gaussview plots of the unoccupied ligand $b_{2g} \pi^*$ combination calculated for Mo₂NN', Mo₂NO', Mo₂NS', Mo₂OO, Mo₂SO and Mo₂SS (drawn with an isosurface value of 0.03).



Center	Atomic	Atomic coordinates (Å)		
number	type	X	У	Z
1	Mo	0.000000	0.000000	1.068605
2	Мо	0.000000	0.000000	-1.068605
3	С	0.000000	2.835663	0.000000
4	С	2.835663	0.000000	0.000000
5	С	-2.835663	0.000000	0.000000
6	С	0.000000	-2.835663	0.000000
7	С	0.000000	4.269333	0.000000
8	С	4.269333	0.000000	0.000000
9	С	-4.269333	0.000000	0.000000
10	С	0.000000	-4.269333	0.000000
11	С	-5.486660	0.000000	0.000000
12	С	0.000000	5.486660	0.000000
13	С	5.486660	0.000000	0.000000
14	С	0.000000	-5.486660	0.000000
15	С	6.911033	0.000000	0.000000
16	С	7.628528	0.000000	-1.213995
17	C	7.628528	0.000000	1.213995
18	C	9.020704	0.000000	-1.208846
19	Н	7.081155	0.000000	-2.151611
20	С	9.020704	0.000000	1.208846
21	Н	7.081155	0.000000	2.151611
22	С	9.722129	0.000000	0.000000
23	Н	9.560997	0.000000	-2.151695
24	Н	9.560997	0.000000	2.151695
25	Н	10.808640	0.000000	0.000000
26	С	-6.911033	0.000000	0.000000
27	С	-7.628528	0.000000	1.213995
28	С	-7.628528	0.000000	-1.213995
29	С	-9.020704	0.000000	1.208846
30	Н	-7.081155	0.000000	2.151611
31	С	-9.020704	0.000000	-1.208846
32	Н	-7.081155	0.000000	-2.151611
33	С	-9.722129	0.000000	0.000000
34	Н	-9.560997	0.000000	2.151695
35	Н	-9.560997	0.000000	-2.151695
36	Н	-10.808640	0.000000	0.000000
37	С	0.000000	6.911033	0.000000
38	C	0.000000	7.628528	1.213995
39	C	0.000000	7.628528	-1.213995
40	С	0.000000	9.020704	1.208846
41	Н	0.000000	7.081155	2.151611
42	С	0.000000	9.020704	-1.208846
43	Н	0.000000	7.081155	-2.151611
44	С	0.000000	9.722129	0.0000000

Table S1. Calculated atomic coordinates for Mo_2NN' .

45	Н	0.000000	9.560997	2.151695
46	Н	0.000000	9.560997	-2.151695
47	Н	0.000000	10.808640	0.000000
48	С	0.000000	-6.911033	0.000000
49	С	0.000000	-7.628528	1.213995
50	С	0.000000	-7.628528	-1.213995
51	C	0.000000	-9.020704	1.208846
52	Н	0.000000	-7.081155	2.151611
53	С	0.000000	-9.020704	-1.208846
54	Н	0.000000	-7.081155	-2.151611
55	С	0.000000	-9.722129	0.000000
56	Н	0.000000	-9.560997	2.151695
57	Н	0.000000	-9.560997	-2.151695
58	Н	0.000000	-10.808640	0.000000
59	Ν	0.000000	2.147150	1.148906
60	Ν	0.000000	2.147150	-1.148906
61	N	2.147150	0.000000	-1.148906
62	N	2.147150	0.000000	1.148906
63	Ν	-2.147150	0.000000	1.148906
64	Ν	-2.147150	0.000000	-1.148906
65	Ν	0.000000	-2.147150	1.148906
66	Ν	0.000000	-2.147150	-1.148906
67	Н	2.739753	0.000000	-1.972711
68	Н	2.739753	0.000000	1.972711
69	Н	0.000000	-2.739753	1.972711
70	Н	0.000000	-2.739753	-1.972711
71	Н	0.000000	2.739753	-1.972711
72	Н	0.000000	2.739753	1.972711
73	Н	-2.739753	0.000000	-1.972711
74	Н	-2.739753	0.000000	1.972711

Center	Atomic	Atomic coordinates (Å)		
number	type	X	У	Z
1	Mo	-0.081500	1.061783	0.000000
2	Mo	0.081500	-1.061783	0.000000
3	С	1.956686	0.024515	1.972556
4	С	-1.956686	-0.024515	1.972556
5	С	1.956686	0.024515	-1.972556
6	С	-1.956686	-0.024515	-1.972556
7	С	2.960416	0.032755	2.995383
8	С	-2.960416	-0.032755	2.995383
9	С	2.960416	0.032755	-2.995383
10	С	-2.960416	-0.032755	-2.995383
11	С	3.812313	0.037561	-3.863458
12	С	3.812313	0.037561	3.863458
13	С	-3.812313	-0.037561	3.863458
14	С	-3.812313	-0.037561	-3.863458
15	С	-4.810924	-0.026715	4.878633
16	С	-5.246020	-1.229052	5.472097
17	С	-5.378869	1.191754	5.303918
18	С	-6.222957	-1.208727	6.463739
19	Η	-4.810151	-2.168674	5.146756
20	С	-6.355247	1.201314	6.296139
21	Н	-5.044759	2.118053	4.847152
22	С	-6.780230	0.003953	6.878752
23	Н	-6.550881	-2.141363	6.914551
24	Н	-6.786554	2.145787	6.616280
25	Н	-7.542509	0.015819	7.652913
26	С	4.810924	0.026715	-4.878633
27	C	5.246020	1.229052	-5.472097
28	С	5.378869	-1.191754	-5.303918
29	C	6.222957	1.208727	-6.463739
30	Н	4.810151	2.168674	-5.146756
31	C	6.355247	-1.201314	-6.296139
32	Н	5.044759	-2.118053	-4.847152
33	С	6.780230	-0.003953	-6.878752
34	Н	6.550881	2.141363	-6.914551
35	Н	6.786554	-2.145787	-6.616280
36	Н	7.542509	-0.015819	-7.652913
37	С	4.810924	0.026715	4.878633
38	С	5.246020	1.229052	5.472097
39	C	5.378869	-1.191754	5.303918
40	C	6.222957	1.208727	6.463739
41	Н	4.810151	2.168674	5.146756
42	C	6.355247	-1.201314	6.296139
43	Н	5.044759	-2.118053	4.847152
44	C	6.780230	-0.003953	6.878752

Table S2. Calculated atomic coordinates for Mo₂NO'.

45	Н	6.550881	2.141363	6.914551
46	Н	6.786554	-2.145787	6.616280
47	Н	7.542509	-0.015819	7.652913
48	С	-4.810924	-0.026715	-4.878633
49	С	-5.378869	1.191754	-5.303918
50	С	-5.246020	-1.229052	-5.472097
51	С	-6.355247	1.201314	-6.296139
52	Н	-5.044759	2.118053	-4.847152
53	С	-6.222957	-1.208727	-6.463739
54	Н	-4.810151	-2.168674	-5.146756
55	С	-6.780230	0.003953	-6.878752
56	Н	-6.786554	2.145787	-6.616280
57	Н	-6.550881	-2.141363	-6.914551
58	Н	-7.542509	0.015819	-7.652913
59	Ν	1.407680	1.155919	1.533425
60	Ν	-1.407680	-1.155919	1.533425
61	Ν	1.407680	1.155919	-1.533425
62	Ν	-1.407680	-1.155919	-1.533425
63	Н	-1.763474	-1.987474	1.997756
64	Н	-1.763474	-1.987474	-1.997756
65	Н	1.763474	1.987474	1.997756
66	Н	1.763474	1.987474	-1.997756
67	0	-1.585765	1.108042	1.474192
68	0	-1.585765	1.108042	-1.474192
69	0	1.585765	-1.108042	-1.474192
70	0	1.585765	-1.108042	1.474192

Center	Atomic	Atomic coordinates (Å)		
number	type	X	у	Z
1	Мо	0.000000	0.000000	1.071142
2	Мо	0.000000	0.000000	-1.071142
3	С	0.000000	3.015014	-0.284333
4	С	3.015014	0.000000	0.284333
5	С	-3.015014	0.000000	0.284333
6	С	0.000000	-3.015014	-0.284333
7	С	0.000000	4.411992	-0.543758
8	С	4.411992	0.000000	0.543758
9	С	-4.411992	0.000000	0.543758
10	С	0.000000	-4.411992	-0.543758
11	С	-5.610241	0.000000	0.760979
12	С	0.000000	5.610241	-0.760979
13	С	5.610241	0.000000	0.760979
14	С	0.000000	-5.610241	-0.760979
15	С	7.012610	0.000000	1.001713
16	С	7.919910	0.000000	-0.077971
17	С	7.515034	0.000000	2.319143
18	С	9.291407	0.000000	0.160049
19	Н	7.534199	0.000000	-1.092575
20	С	8.888355	0.000000	2.546082
21	Н	6.818431	0.000000	3.151835
22	С	9.779938	0.000000	1.469672
23	Н	9.982108	0.000000	-0.678640
24	Н	9.264822	0.000000	3.565268
25	Н	10.851255	0.000000	1.650669
26	С	-7.012610	0.000000	1.001713
27	С	-7.515034	0.000000	2.319143
28	С	-7.919910	0.000000	-0.077971
29	С	-8.888355	0.000000	2.546082
30	Н	-6.818431	0.000000	3.151835
31	С	-9.291407	0.000000	0.160049
32	Н	-7.534199	0.000000	-1.092575
33	С	-9.779938	0.000000	1.469672
34	Н	-9.264822	0.000000	3.565268
35	Н	-9.982108	0.000000	-0.678640
36	Н	-10.851255	0.000000	1.650669
37	С	0.000000	7.012610	-1.001713
38	С	0.000000	7.919910	0.077971
39	С	0.000000	7.515034	-2.319143
40	С	0.000000	9.291407	-0.160049
41	Н	0.000000	7.534199	1.092575
42	С	0.000000	8.888355	-2.546082
43	тт	0.000000	6 0 1 0 1 2 1	2 151925
	H	0.000000	0.818431	-5.151655

Table S3. Calculated atomic coordinates for Mo_2NS' .

45	Н	0.000000	9.982108	0.678640
46	Н	0.000000	9.264822	-3.565268
47	Н	0.000000	10.851255	-1.650669
48	С	0.000000	-7.012610	-1.001713
49	C	0.000000	-7.919910	0.077971
50	C	0.000000	-7.515034	-2.319143
51	С	0.000000	-9.291407	-0.160049
52	Н	0.000000	-7.534199	1.092575
53	C	0.000000	-8.888355	-2.546082
54	Н	0.000000	-6.818431	-3.151835
55	С	0.000000	-9.779938	-1.469672
56	Н	0.000000	-9.982108	0.678640
57	Н	0.000000	-9.264822	-3.565268
58	Н	0.000000	-10.851255	-1.650669
59	N	0.000000	2.131213	-1.269055
60	N	2.131213	0.000000	1.269055
61	N	-2.131213	0.000000	1.269055
62	N	0.000000	-2.131213	-1.269055
63	Н	2.575331	0.000000	2.188170
64	Н	0.000000	-2.575331	-2.188170
65	Н	0.000000	2.575331	-2.188170
66	Н	-2.575331	0.000000	2.188170
67	S	0.000000	2.488422	1.368915
68	S	0.000000	-2.488422	1.368915
69	S	-2.488422	0.000000	-1.368915
70	S	2.488422	0.000000	-1.368915

Center	Atomic	Atomic coordinates (Å)		
number	type	X	у	Z
1	Mo	0.000000	0.000000	1.062083
2	Мо	0.000000	0.000000	-1.062083
3	С	0.000000	2.727679	0.000000
4	С	2.727679	0.000000	0.000000
5	С	-2.727679	0.000000	0.000000
6	С	0.000000	-2.727679	0.000000
7	0	2.102730	0.000000	1.122333
8	0	2.102730	0.000000	-1.122333
9	0	0.000000	-2.102730	-1.122333
10	0	0.000000	-2.102730	1.122333
11	0	-2.102730	0.000000	1.122333
12	0	-2.102730	0.000000	-1.122333
13	0	0.000000	2.102730	-1.122333
14	0	0.000000	2.102730	1.122333
15	С	0.000000	4.155032	0.000000
16	С	4.155032	0.000000	0.000000
17	С	-4.155032	0.000000	0.000000
18	С	0.000000	-4.155032	0.000000
19	С	-5.370701	0.000000	0.000000
20	С	0.000000	5.370701	0.000000
21	С	5.370701	0.000000	0.000000
22	С	0.000000	-5.370701	0.000000
23	С	6.793215	0.000000	0.000000
24	С	7.505672	0.000000	-1.216485
25	С	7.505672	0.000000	1.216485
26	С	8.897547	0.000000	-1.210765
27	Н	6.955395	0.000000	-2.152146
28	С	8.897547	0.000000	1.210765
29	Н	6.955395	0.000000	2.152146
30	С	9.596178	0.000000	0.000000
31	Н	9.439491	0.000000	-2.152304
32	Н	9.439491	0.000000	2.152304
33	Н	10.682699	0.000000	0.000000
34	С	-6.793215	0.000000	0.000000
35	С	-7.505672	0.000000	1.216485
36	С	-7.505672	0.000000	-1.216485
37	С	-8.897547	0.000000	1.210765
38	Н	-6.955395	0.000000	2.152146
39	С	-8.897547	0.000000	-1.210765
40	Н	-6.955395	0.000000	-2.152146
41	С	-9.596178	0.000000	0.000000
42	Н	-9.439491	0.000000	2.152304
43	Н	-9.439491	0.000000	-2.152304
44	Н	-10.682699	0.000000	0.000000

Table S4. Calculated atomic coordinates for Mo_2OO .

45	С	0.000000	6.793215	0.000000
46	С	0.000000	7.505672	1.216485
47	С	0.000000	7.505672	-1.216485
48	С	0.000000	8.897547	1.210765
49	Н	0.000000	6.955395	2.152146
50	C	0.000000	8.897547	-1.210765
51	Н	0.000000	6.955395	-2.152146
52	С	0.000000	9.596178	0.000000
53	Н	0.000000	9.439491	2.152304
54	Н	0.000000	9.439491	-2.152304
55	Н	0.000000	10.682699	0.000000
56	С	0.000000	-6.793215	0.000000
57	С	0.000000	-7.505672	1.216485
58	С	0.000000	-7.505672	-1.216485
59	С	0.000000	-8.897547	1.210765
60	Н	0.000000	-6.955395	2.152146
61	С	0.000000	-8.897547	-1.210765
62	Н	0.000000	-6.955395	-2.152146
63	С	0.000000	-9.596178	0.000000
64	Н	0.000000	-9.439491	2.152304
65	Н	0.000000	-9.439491	-2.152304
66	Н	0.000000	-10.682699	0.000000

Center	Atomic	Atomic coordinates (Å)		
number	type	X	У	Z
1	Мо	0.000000	0.000000	1.078219
2	Мо	0.000000	0.000000	-1.078219
3	С	0.000000	2.934979	-0.418522
4	С	2.934979	0.000000	0.418522
5	С	-2.934979	0.000000	0.418522
6	С	0.000000	-2.934979	-0.418522
7	S	0.000000	-2.488713	1.252747
8	S	-2.488713	0.000000	-1.252747
9	С	0.000000	4.311042	-0.757865
10	С	4.311042	0.000000	0.757865
11	С	-4.311042	0.000000	0.757865
12	С	0.000000	-4.311042	-0.757865
13	С	-5.496320	0.000000	1.038683
14	С	0.000000	5.496320	-1.038683
15	С	5.496320	0.000000	1.038683
16	С	0.000000	-5.496320	-1.038683
17	С	6.879525	0.000000	1.363765
18	С	7.851618	0.000000	0.341720
19	С	7.295581	0.000000	2.711396
20	С	9.205147	0.000000	0.665430
21	Н	7.529616	0.000000	-0.694874
22	С	8.651790	0.000000	3.023365
23	Н	6.546221	0.000000	3.496658
24	С	9.608505	0.000000	2.003956
25	Н	9.947946	0.000000	-0.127280
26	Н	8.964618	0.000000	4.063713
27	Н	10.666272	0.000000	2.252231
28	С	-6.879525	0.000000	1.363765
29	С	-7.295581	0.000000	2.711396
30	С	-7.851618	0.000000	0.341720
31	С	-8.651790	0.000000	3.023365
32	Н	-6.546221	0.000000	3.496658
33	С	-9.205147	0.000000	0.665430
34	Н	-7.529616	0.000000	-0.694874
35	С	-9.608505	0.000000	2.003956
36	Н	-8.964618	0.000000	4.063713
37	Н	-9.947946	0.000000	-0.127280
38	Н	-10.666272	0.000000	2.252231
39	С	0.000000	6.879525	-1.363765
40	С	0.000000	7.851618	-0.341720
41	С	0.000000	7.295581	-2.711396
42	С	0.000000	9.205147	-0.665430
43	Н	0.000000	7.529616	0.694874
44	С	0.000000	8.651790	-3.023365

Table S5. Calculated atomic coordinates for Mo_2SO .

45	Н	0.000000	6.546221	-3.496658
46	С	0.000000	9.608505	-2.003956
47	Н	0.000000	9.947946	0.127280
48	Н	0.000000	8.964618	-4.063713
49	Н	0.000000	10.666272	-2.252231
50	С	0.000000	-6.879525	-1.363765
51	C	0.000000	-7.851618	-0.341720
52	C	0.000000	-7.295581	-2.711396
53	С	0.000000	-9.205147	-0.665430
54	Н	0.000000	-7.529616	0.694874
55	С	0.000000	-8.651790	-3.023365
56	Н	0.000000	-6.546221	-3.496658
57	С	0.000000	-9.608505	-2.003956
58	Н	0.000000	-9.947946	0.127280
59	Н	0.000000	-8.964618	-4.063713
60	Н	0.000000	-10.666272	-2.252231
61	S	0.000000	2.488713	1.252747
62	S	2.488713	0.000000	-1.252747
63	0	2.059846	0.000000	1.351112
64	0	-2.059846	0.000000	1.351112
65	0	0.000000	-2.059846	-1.351112
66	0	0.000000	2.059846	-1.351112

Center	Atomic	Atomic coordinates (Å)		
number	type	X	У	Z
1	Мо	0.000000	0.000000	1.075063
2	Mo	0.000000	0.000000	-1.075063
3	С	0.000000	3.256081	0.000000
4	С	3.256081	0.000000	0.000000
5	С	-3.256081	0.000000	0.000000
6	С	0.000000	-3.256081	0.000000
7	S	2.456765	0.000000	1.514827
8	S	2.456765	0.000000	-1.514827
9	S	0.000000	-2.456765	-1.514827
10	S	0.000000	-2.456765	1.514827
11	S	-2.456765	0.000000	1.514827
12	S	-2.456765	0.000000	-1.514827
13	S	0.000000	2.456765	-1.514827
14	S	0.000000	2.456765	1.514827
15	С	0.000000	4.662480	0.000000
16	С	4.662480	0.000000	0.000000
17	С	-4.662480	0.000000	0.000000
18	С	0.000000	-4.662480	0.000000
19	С	-5.882504	0.000000	0.000000
20	С	0.000000	5.882504	0.000000
21	С	5.882504	0.000000	0.000000
22	С	0.000000	-5.882504	0.000000
23	С	7.301810	0.000000	0.000000
24	С	8.015529	0.000000	-1.217197
25	С	8.015529	0.000000	1.217197
26	С	9.406973	0.000000	-1.211023
27	Н	7.465477	0.000000	-2.152939
28	С	9.406973	0.000000	1.211023
29	Н	7.465477	0.000000	2.152939
30	С	10.105670	0.000000	0.000000
31	Н	9.949128	0.000000	-2.152424
32	Н	9.949128	0.000000	2.152424
33	Н	11.192162	0.000000	0.000000
34	С	-7.301810	0.000000	0.000000
35	С	-8.015529	0.000000	1.217197
36	С	-8.015529	0.000000	-1.217197
37	С	-9.406973	0.000000	1.211023
38	Н	-7.465477	0.000000	2.152939
39	С	-9.406973	0.000000	-1.211023
40	Н	-7.465477	0.000000	-2.152939
41	C	-10.105670	0.000000	0.000000
42	Н	-9.949128	0.000000	2.152424
43	Н	-9.949128	0.000000	-2.152424
44	Н	-11.192162	0.000000	0.000000

Table S6. Calculated atomic coordinates for Mo_2SS .

45	С	0.000000	7.301810	0.000000
46	С	0.000000	8.015529	1.217197
47	С	0.000000	8.015529	-1.217197
48	С	0.000000	9.406973	1.211023
49	Н	0.000000	7.465477	2.152939
50	С	0.000000	9.406973	-1.211023
51	Н	0.000000	7.465477	-2.152939
52	С	0.000000	10.105670	0.000000
53	Н	0.000000	9.949128	2.152424
54	Н	0.000000	9.949128	-2.152424
55	Н	0.000000	11.192162	0.000000
56	С	0.000000	-7.301810	0.000000
57	С	0.000000	-8.015529	1.217197
58	С	0.000000	-8.015529	-1.217197
59	С	0.000000	-9.406973	1.211023
60	Н	0.000000	-7.465477	2.152939
61	С	0.000000	-9.406973	-1.211023
62	Н	0.000000	-7.465477	-2.152939
63	С	0.000000	-10.105670	0.000000
64	Н	0.000000	-9.949128	2.152424
65	Н	0.000000	-9.949128	-2.152424
66	Н	0.000000	-11.192162	0.000000