**Supporting Information**

**Table S1** Coordinates used in the DFT calculations for $[MoO(SMe)_4]^-$ in $C_4$ symmetry with a O-Mo-S-C(α) dihedral angle = 58.8°

| | x | y | z |
|---|---|---|---|
| Mo | 0.0000 | 0.0000 | 0.0000 |
| O | 0.0000 | 0.0000 | 1.6690 |
| S | 2.2590 | 0.0000 | -0.8160 |
| S | 0.0000 | -2.2590 | -0.8160 |
| S | -2.2590 | 0.0000 | -0.8160 |
| S | 0.0000 | 2.2590 | -0.8160 |
| C | 1.4170 | 3.1120 | -0.2120 |
| C | -3.1120 | 1.4170 | -0.2120 |
| C | 3.1120 | -1.4170 | -0.2120 |
| C | -1.4170 | -3.1120 | -0.2120 |
| H | -3.4550 | 2.0240 | -1.0570 |
| H | -2.4350 | 2.0100 | 0.4150 |
| H | -3.9750 | 1.0970 | 0.3830 |
| H | 2.0240 | 3.4550 | -1.0570 |
| H | 2.0100 | 2.4350 | 0.4150 |
| H | 1.0970 | 3.9750 | 0.3830 |
| H | 3.9750 | -1.0970 | 0.3830 |
| H | 3.4550 | -2.0240 | -1.0570 |
| H | 2.4350 | -2.0100 | 0.4150 |
| H | -2.0100 | -2.4350 | 0.4150 |
| H | -1.0970 | -3.9750 | 0.3830 |
| H | -2.0240 | -3.4550 | -1.0570 |

**Table S2** Coordinates used in the DFT calculations for $[MoO(edt)_2]^-$ in $C_{2v}$ symmetry.

| | x | y | z |
|---|---|---|---|
| Mo | 0.0000 | 0.0000 | 0.0000 |
| O | 0.0000 | 0.0000 | 1.6780 |
| S | -1.5912 | 1.5857 | -0.7647 |
| S | 1.5912 | 1.5857 | -0.7647 |
| C | -0.6611 | 3.0568 | -1.0264 |
| C | 0.6611 | 3.0568 | -1.0264 |
| S | 1.5912 | -1.5857 | -0.7647 |
| S | -1.5912 | -1.5857 | -0.7647 |
| C | 0.6611 | -3.0568 | -1.0264 |
| C | -0.6611 | -3.0568 | -1.0264 |
| H | -0.9325 | 3.3897 | -1.8849 |
| H | 0.9325 | 3.3897 | -1.8849 |
| H | 0.9325 | -3.3897 | -1.8849 |
| H | -0.9325 | -3.3897 | -1.8849 |
| H | -0.9325 | 3.6176 | -0.2961 |
| H | 0.9325 | 3.6176 | -0.2961 |
| H | 0.9325 | -3.6176 | -0.2961 |
| H | -0.9325 | -3.6176 | -0.2961 |

**Table S3.** Results of unrestricted DFT calculations for the frontier orbitals of $[MoO(edt)_2]^-$.[a]

| Molecular Orbital Symmetry | Energy /eV | Composition /% | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Mo | | | | | O | | | S | | |
| $C_{2v}$ | | $4d_{z^2}$ | $4d_{x^2-y^2}$ | $4d_{xy}$ | $4d_{xz}$ | $4d_{yz}$ | $2p_x$ | $2p_y$ | $2p_z$ | $3p_x$ | $3p_y$ | $3p_z$ |
| $8a_1$ (pseudo-σ) | -2.517 | 1.5 | 5.3 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 4.1 | 53.9 | 5.0 | 9.5 |
| $5a_2$ (pseudo-σ) | -2.369 | 0.0 | 0.0 | 10.8 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 65.3 | 0.8 | 0.9 |
| $7b_2$ (pseudo-σ) | -1.653 | 0.0 | 0.0 | 0.0 | 0.0 | 4.5 | 0.0 | 13.4 | 0.0 | 58.3 | 12.7 | 2.8 |
| $9a_1$ (π) | -1.588 | 1.7 | 0.1 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 7.5 | 9.3 | 9.8 | 64.2 |
| $6b_1$ (pseudo-σ) | -1.498 | 0.0 | 0.0 | 0.0 | 3.7 | 0.0 | 12.6 | 0.0 | 0.0 | 67.2 | 14.7 | 0.2 |
| $8b_2$ (π) | -0.865 | 0.0 | 0.0 | 0.0 | 0.0 | 2.0 | 0 | 6.5 | 0.0 | 0.0 | 2.5 | 84.3 |
| $7b_1$ (π) | -0.670 | 0.0 | 0.0 | 0.0 | 3.0 | 0.0 | 4.3 | 0.0 | 0.0 | 1.4 | 0.1 | 82.8 |
| **$6a_2$ (π)** | **-0.112** | **0.0** | **0.0** | **1.2** | **0.0** | **0.0** | **0.0** | **0.0** | **0.0** | **4.8** | **15.0** | **69.3** |
| $10a_1$ ($4d_{x^2-y^2}$) | 0.000 | 0.2 | 74.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.3 | 1.9 | 1.0 | 1.5 |
| $8b_1$ ($4d_{xz}$) | 2.711 | 0.0 | 0.0 | 0.0 | 55.6 | 0.0 | 19.4 | 0.0 | 0.0 | 5.1 | 10.3 | 2.3 |
| $9b_2$ ($4d_{yz}$) | 2.796 | 0.0 | 0.0 | 0.0 | 0.0 | 54.2 | 0.0 | 18.9 | 0.0 | 10.4 | 7.6 | 2.4 |
| $7a_2$ ($4d_{xy}$) | 3.616 | 0.0 | 0.0 | 44.1 | 0.0 | 0.0 | 0.0 | 0 | 0.0 | 12.6 | 16.9 | 8.7 |
| $11a_1$ ($4d_{z^2}$) | 3.709 | 6.3 | 0.3 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 2.2 | 0.4 | 0.1 | 2.2 |

a) The compositions and energies are for the β spin orbitals. The highest occupied molecular orbital (HOMO) is shown in bold.