Supporting Information

Metal-Sulfur Valence Orbital Interaction Energies in Metal–Dithiolene Complexes: Determination of Charge and Overlap Interaction Energies by Comparison of Core and Valence Ionization Energy Shifts

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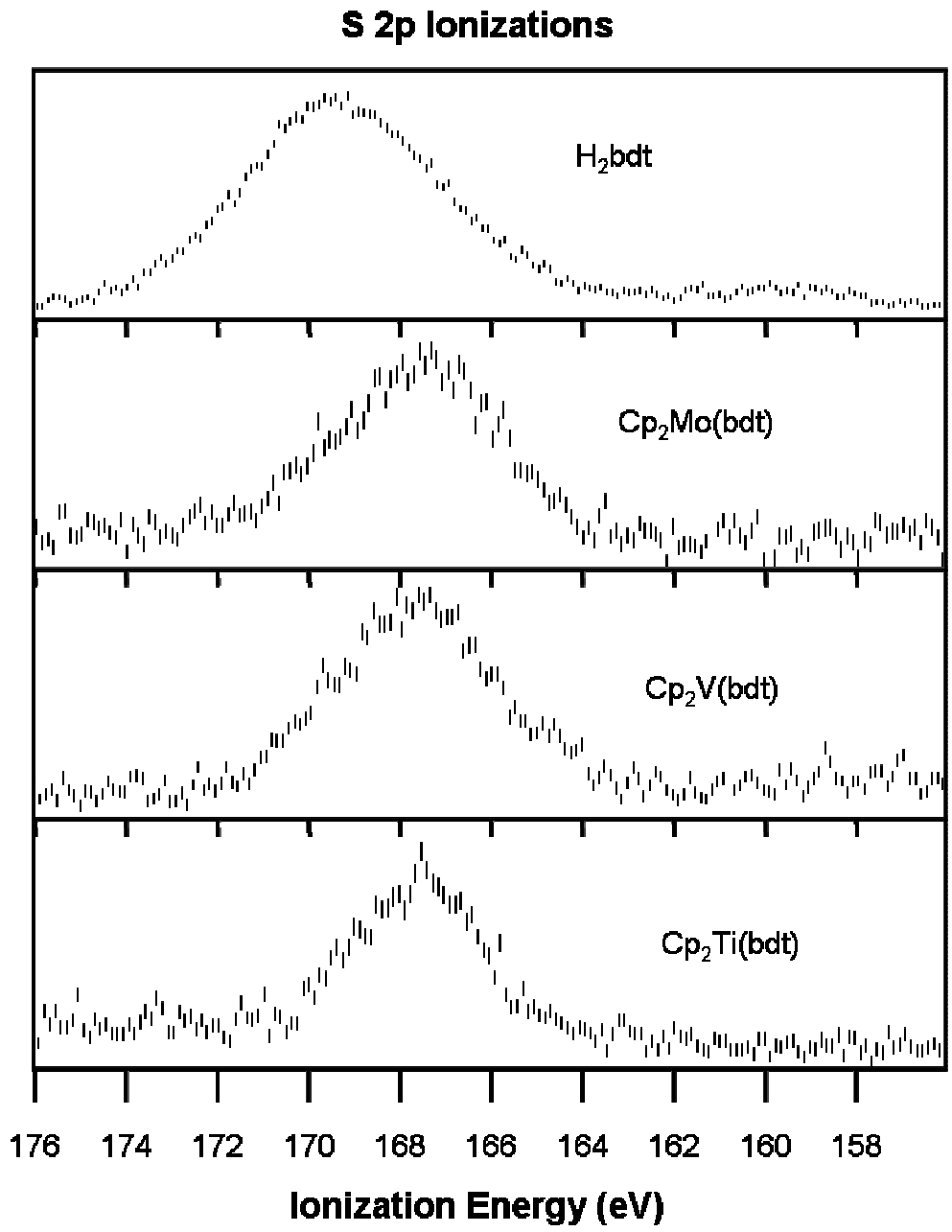

Figure S1. The summed X-ray photoelectron spectra of the S 2p region for the benzene dithiol and the series $Cp_2M(bdt)$ where M = Mo, V & Ti and bdt = benzenedithiolate.

Table S1. S $2p_{3/2}$ Ionization energies.

Scan	H_2bdt	Cp_2Mo(bdt)	Cp_2V(bdt)	Cp_2Ti(bdt)
1	169.258	167.437	167.084	167.264
2	169.321	167.567	167.067	167.627
3	169.371	166.961	166.926	167.376
4	169.236	167.315	167.124	167.408
5	169.476	167.158	167.016	167.581
6	169.321	167.173	167.243	167.311
7	169.442	167.240	167.107	167.318
8	169.101	167.061	167.390	--
9	169.247	167.116	167.441	--
10	169.272	167.365	167.261	--
11	169.204	167.329	167.343	--
12	169.118	--	--	--
AVG	169.281	167.247	167.182	167.412
STDEV	0.114	0.176	0.165	0.140

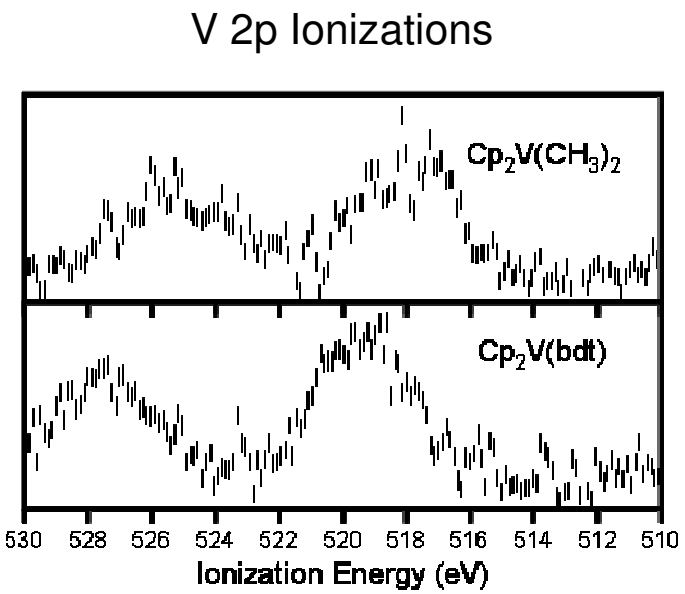

Figure S2. The summed X-ray photoelectron spectra of the V 2p region for $Cp_2V(CH_3)_2$ and $Cp_2V(bdt)$.

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Table S2. V $2p_{3/2}$ ionization energies

Scan	$Cp_2V(CH_3)_2$	$Cp_2V(bdt)$
1	518.155	519.071
2	518.720	519.337
3	519.033	519.522
4	518.913	519.558
5	518.684	519.512
6	518.684	519.535
7	518.606	519.169
8	--	519.179
9	--	519.277
AVG	518.685	519.351
STDEV	0.277	0.187

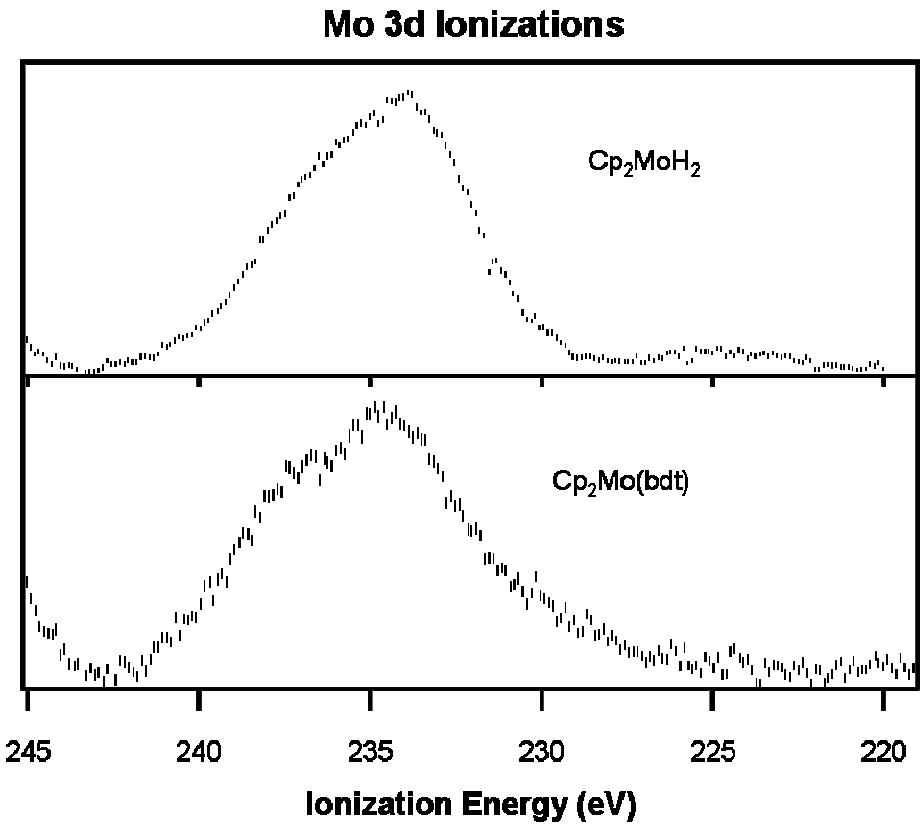

Figure S3. The summed X-ray photoelectron spectra of the Mo 3d region for Cp_2MoH_2 and $Cp_2Mo(bdt)$.

Table S3. Mo $3d_{5/2}$ ionization energies

Scan	Cp_2MoH_2	$Cp_2Mo(bdt)$
1	233.834	234.633
2	233.743	234.580
3	234.010	234.423
4	233.932	234.66
5	233.872	234.440
6	234.102	234.532
7	234.113	234.560
8	234.103	234.446
9	234.056	234.628
10	233.984	234.611
11	233.895	234.812
12	233.897	234.578
13	233.874	--
14	233.848	--
AVG	233.947	234.575
STDEV	0.116	0.110

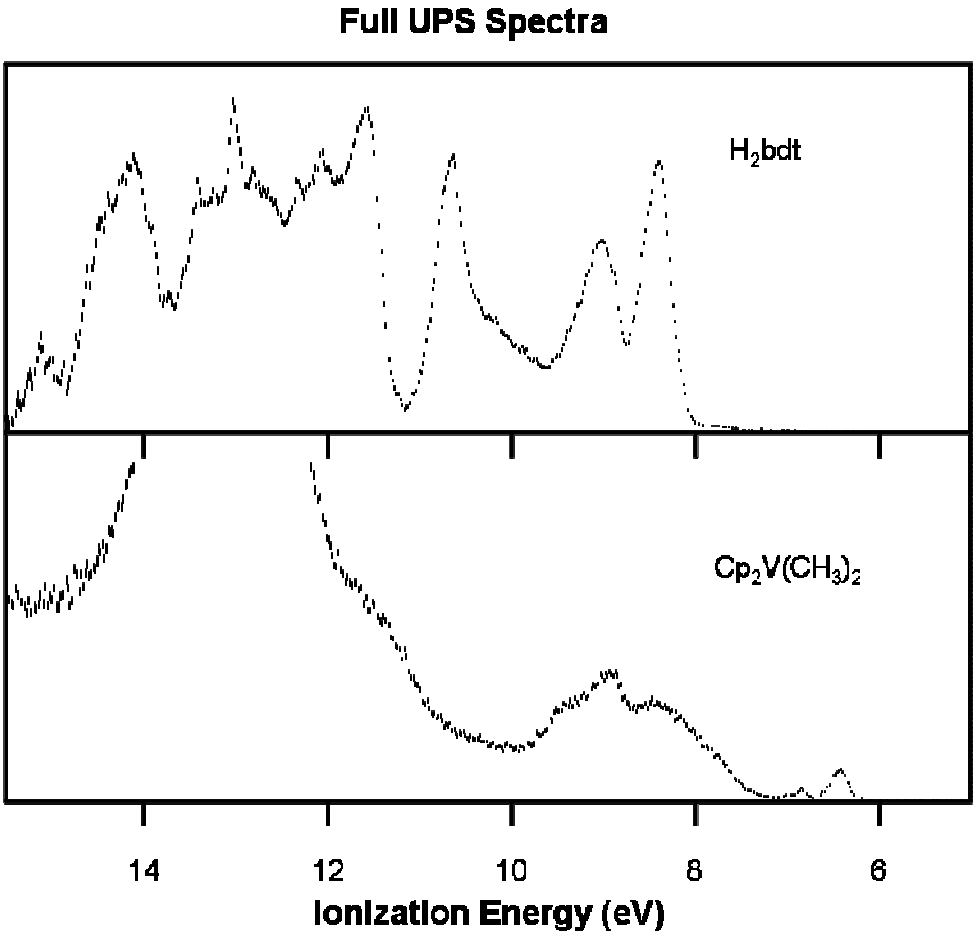

Figure S4. The UV photoelectron spectrum of benzenedithiol and $Cp_2V(CH_3)_2$.

Coordinates used for orbital plots

$Cp_2Mo(bdt)$

Mo	0.026407	0.027731	0.000000
S	1.850842	0.103266	-1.599475
S	1.850842	0.103266	1.599475
C	3.387102	0.116332	-0.703132
C	3.387102	0.116332	0.703132
C	4.609234	0.138632	-1.397615
C	4.609234	0.138632	1.397615
C	5.818029	0.162140	-0.701021
C	5.818029	0.162140	0.701021
H	4.601483	0.138479	-2.489024
H	4.601483	0.138479	2.489024
H	6.759954	0.180268	-1.251081
H	6.759954	0.180268	1.251081
C	0.168724	2.359303	0.000000
C	-0.604367	2.031032	-1.161273
C	-0.604367	2.031032	1.161273
C	-1.842839	1.506993	-0.713669
C	-1.842839	1.506993	0.713669
H	1.167377	2.778413	0.000000
H	-0.300286	2.173998	-2.192573
H	-0.300286	2.173998	2.192573
H	-2.640533	1.135572	-1.351086
H	-2.640533	1.135572	1.351086
C	-1.809641	-1.444325	0.000000
C	-1.037117	-1.768090	-1.164235
C	-1.037117	-1.768090	1.164235
C	0.175092	-2.368457	-0.703505
C	0.175092	-2.368457	0.703505
H	-2.817812	-1.047564	0.000000
H	-1.349648	-1.674010	-2.199713
H	-1.349648	-1.674010	2.199713
H	0.997592	-2.694490	-1.330462
H	0.997592	-2.694490	1.330462

$Cp_2V(bdt)$

V	0.057598	-0.099107	0.000000
S	1.866425	-0.440368	-1.588724
S	1.866425	-0.440368	1.588724
C	3.276049	0.165119	-0.709854
C	3.276049	0.165119	0.709854
C	4.428978	0.584316	-1.398939
C	4.428978	0.584316	1.398939
C	5.569383	0.981610	-0.701313
C	5.569383	0.981610	0.701313
H	4.420708	0.587197	-2.489772
H	4.420708	0.587197	2.489772
H	6.457483	1.296662	-1.250775
H	6.457483	1.296662	1.250775
C	0.752999	2.141760	0.000000
C	-0.062921	1.964358	-1.154142
C	-0.062921	1.964358	1.154142
C	-1.369030	1.651322	-0.717223
C	-1.369030	1.651322	0.717223
H	1.817396	2.353242	0.000000
H	0.272748	2.021584	-2.183613
H	0.272748	2.021584	2.183613
H	-2.221239	1.443371	-1.357452
H	-2.221239	1.443371	1.357452
C	-2.043182	-1.143744	0.000000
C	-1.339710	-1.591759	-1.154854
C	-1.339710	-1.591759	1.154854
C	-0.230446	-2.363491	-0.708587
C	-0.230446	-2.363491	0.708587
H	-2.953043	-0.553214	0.000000
H	-1.613429	-1.406118	-2.189486
H	-1.613429	-1.406118	2.189486
H	0.511654	-2.841976	-1.336841
H	0.511654	-2.841976	1.336841

$Cp_2Ti(bdt)$

Ti	0.126858	-0.131872	0.000000
S	1.881639	-0.590684	-1.584868
S	1.881639	-0.590684	1.584868
C	3.191652	0.156002	-0.713063
C	3.191652	0.156002	0.713063
C	4.300951	0.686837	-1.394486
C	4.300951	0.686837	1.394486
C	5.388365	1.191151	-0.699974
C	5.388365	1.191151	0.699974
H	4.294028	0.690765	-2.482834
H	4.294028	0.690765	2.482834
H	6.243254	1.587206	-1.247123
H	6.243254	1.587206	1.247123
C	0.881576	2.171894	0.000000
C	0.071717	1.993466	-1.146287
C	0.071717	1.993466	1.146287
C	-1.235240	1.693045	-0.712906
C	-1.235240	1.693045	0.712906
H	1.936811	2.409294	0.000000
H	0.402257	2.060415	-2.176345
H	0.402257	2.060415	2.176345
H	-2.090345	1.509334	-1.354379
H	-2.090345	1.509334	1.354379
C	-2.044901	-1.089039	0.000000
C	-1.371878	-1.575999	-1.146211
C	-1.371878	-1.575999	1.146211
C	-0.296945	-2.386238	-0.708015
C	-0.296945	-2.386238	0.708015
H	-2.926578	-0.460019	0.000000
H	-1.633981	-1.371296	-2.179329
H	-1.633981	-1.371296	2.179329
H	0.403296	-2.922032	-1.336168
H	0.403296	-2.922032	1.336168

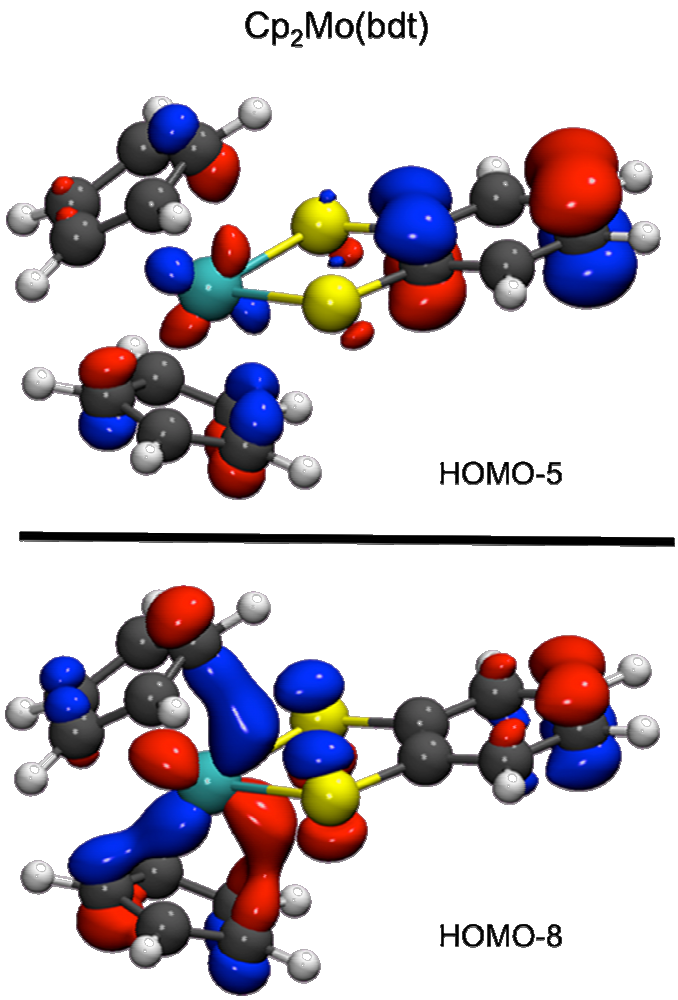

Figure S5. The calculated HOMO-5 and HOMO-8 of $Cp_2Mo(bdt)$ showing a nonbonding and bonding interaction between the Cp rings' π-system and the dithiolene $S_{\pi+}$. Their Kohn-Sham orbital energies were found to be 2.6 and 3.2 eV more stable than the HOMO of the molecule.

Coordinates for distorted H_2bdt structure

C	0.000000	-0.698041	5.816643
C	0.000000	0.698042	5.816643
C	0.000000	1.389426	4.610311
C	0.000000	0.703943	3.391973
C	0.000000	-0.703943	3.391973
C	0.000000	-1.389426	4.610311
S	0.000000	1.956100	2.139816
S	0.000000	-1.956100	2.139816
H	0.237192	-2.986950	3.011340
H	0.237192	2.986950	3.011338
H	0.000000	-1.256437	6.765405
H	0.000000	1.256438	6.765405
H	0.000000	-2.492702	4.603476
H	0.000000	2.492702	4.603475

Table S4. Calculated vertical ionization energies for H_2bdt structures in eV.

Compound	ΔSCF[a]
H_2bdt	7.80
H_2bdt – distorted[b]	7.74

[a] Calculated as the difference in the SCF of the neutral and cationic structure of the same geometry. [b] H_2bdt with a lengthened S-S distance of 3.91Å and with the S-pπ orbitals bent out of plane by 10°.