Electronic Supplementary Information for

$Sc_2S@C_{68}$: an Obtuse Di-scandium Sulfide Cluster Trapped in a C_{2v} Fullerene Cage

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I. Fullerene anions screened at AM1 level.

The total number of these isomers is 2636. Here we only provide the isomers with the relative energy less than 50 kcal/mol. For other results, please contact the corresponding author.

Table S1. C_{68}^{2-} anions screened at AM1 level.

Spiral Number	PA[a]	Symmetry	Charge	Heat of Formation (kcal/mol)	ΔH_f (kcal/mol)
6094	2	*Cs*	-2	965.9964	0.00
6195	2	*C2*	-2	970.48287	4.49
6073	2	*C2v*	-2	971.05931	5.06
6146	2	*C2*	-2	971.9478	5.95
6148	2	*C1*	-2	977.6262	11.63
6328	2	*C2*	-2	977.7805	11.78
6198	2	*C1*	-2	978.00023	12.00
6149	2	*C2*	-2	983.04311	17.05
6319	3	*C1*	-2	993.88645	27.89
6075	3	*C1*	-2	993.89096	27.89
6290	2	*C2*	-2	993.89676	27.90
6079	3	*C1*	-2	994.33275	28.34
6128	3	*C1*	-2	994.84979	28.85
6050	3	*C1*	-2	994.87345	28.88
6101	3	*C1*	-2	995.51938	29.52
6228	3	*C1*	-2	995.61919	29.62
6232	3	*C1*	-2	996.72809	30.73
6097	3	*C1*	-2	997.06569	31.07
5615	3	*C1*	-2	997.5574	31.56
6309	3	*C1*	-2	997.60492	31.61
6102	3	*C1*	-2	998.00878	32.01
6070	3	*C1*	-2	998.23924	32.24
6174	3	*C1*	-2	998.27718	32.28
5205	3	*C1*	-2	998.39174	32.40
6029	3	*C1*	-2	998.39409	32.40
6117	3	*C1*	-2	998.53105	32.53
6089	3	*C2*	-2	999.41318	33.42
6088	3	*C1*	-2	999.5321	33.54
6147	3	*C1*	-2	999.8039	33.81
6116	3	*C1*	-2	1000.12028	34.12
6193	3	*C2*	-2	1000.18379	34.19
6192	3	*C1*	-2	1000.52802	34.53
6201	3	*C1*	-2	1000.6714	34.68
6127	3	*C1*	-2	1001.54113	35.54
6270	2	*C1*	-2	1002.62879	36.63
6230	3	*C1*	-2	1002.77872	36.78

6160	3	*C1*	-2	1002.92715	36.93
5596	3	*C1*	-2	1003.12287	37.13
6138	3	*C1*	-2	1003.14575	37.15
6072	3	*Cs*	-2	1003.35255	37.36
6150	3	*C1*	-2	1003.73711	37.74
6154	3	*C1*	-2	1004.00199	38.01
4822	3	*C1*	-2	1006.36071	40.36
6301	3	*C1*	-2	1006.37676	40.38
6162	3	*C1*	-2	1006.46141	40.47
6108	3	*C2*	-2	1006.63581	40.64
6039	3	*C1*	-2	1007.37497	41.38
4817	3	*C1*	-2	1007.62514	41.63
6118	3	*C2*	-2	1008.23685	42.24
6166	3	*C1*	-2	1009.56518	43.57
6153	3	*C1*	-2	1009.64506	43.65
6145	3	*C1*	-2	1010.65071	44.65
3824	3	*C2*	-2	1010.94983	44.95
5996	3	*C1*	-2	1011.32401	45.33
6063	3	*C1*	-2	1011.57198	45.58
6269	2	*D2*	-2	1012.59562	46.60
6329	3	*C3*	-2	1013.22613	47.23
6110	3	*C1*	-2	1013.33994	47.34
6031	4	*C1*	-2	1014.23708	48.24
6095	4	*C1*	-2	1014.41077	48.41
6271	3	*C2*	-2	1014.87344	48.88
6291	3	*C1*	-2	1015.19032	49.19
6229	4	*C2*	-2	1015.76129	49.76

[a] PA means the number of pentagon adjacencies.

Table S2. C_{68}^{4-} anions screened at AM1 level.

Spiral Number	Symmetry	Charge	PA[a]	Heat of Formation (kcal/mol)	ΔH_f (kcal/mol)
6073	C2v	-4	2	1120.3404	0.00
6140	D3	-4	3	1133.38459	13.04
6146	C2	-4	2	1134.85258	14.51
6118	C2	-4	3	1135.14825	14.81
6116	C1	-4	3	1136.90853	16.57
6039	C1	-4	3	1137.43507	17.09
6072	Cs	-4	3	1138.87345	18.53
6079	C1	-4	3	1139.80143	19.46
6094	Cs	-4	2	1139.86589	19.53
6102	C1	-4	3	1142.09362	21.75
6148	C1	-4	2	1142.11652	21.78
6101	C1	-4	3	1145.77171	25.43

6195	C2	-4	2	1148.17864	27.84
6138	C1	-4	3	1148.3464	28.01
6117	C1	-4	3	1148.41571	28.08
6075	C1	-4	3	1148.62572	28.29
6081	Cs	-4	4	1148.83901	28.50
6070	C1	-4	3	1149.55781	29.22
6110	C1	-4	3	1150.53	30.19
6080	C1	-4	4	1150.7922	30.45
6128	C1	-4	3	1150.86921	30.53
6088	C1	-4	3	1151.71578	31.38
6309	C1	-4	3	1151.94135	31.60
5596	C1	-4	3	1152.34386	32.00
6089	C2	-4	3	1152.35467	32.01
6290	C2	-4	2	1152.78602	32.45
5615	C1	-4	3	1153.89894	33.56
6050	C1	-4	3	1154.06787	33.73
6099	D2	-4	4	1154.6557	34.32
6228	C1	-4	3	1155.24162	34.90
6149	C2	-4	2	1155.35634	35.02
6107	C1	-4	4	1156.47772	36.14
6328	C2	-4	2	1156.5543	36.21
6041	C1	-4	4	1156.91122	36.57
6198	C1	-4	2	1157.5441	37.20
5626	Cs	-4	4	1157.61131	37.27
6104	C1	-4	4	1157.90589	37.57
6060	C1	-4	4	1158.85593	38.52
6127	C1	-4	3	1158.91526	38.57
6108	C2	-4	3	1159.63864	39.30
5087	Cs	-4	4	1159.92541	39.59
6193	C2	-4	3	1160.04567	39.71
6147	C1	-4	3	1160.18742	39.85
6160	C1	-4	3	1160.52449	40.18
6112	C1	-4	4	1161.09993	40.76
6114	C1	-4	4	1161.18271	40.84
6229	C2	-4	4	1161.32226	40.98
6097	C1	-4	3	1161.39202	41.05
6318	D2	-4	4	1161.3962	41.06
6201	C1	-4	3	1161.72947	41.39
6095	C1	-4	4	1161.73467	41.39
6042	C1	-4	4	1162.52177	42.18
5996	C1	-4	3	1162.7314	42.39
6096	C1	-4	4	1162.87824	42.54
6043	C1	-4	4	1163.35819	43.02
6154	C1	-4	3	1163.54388	43.20

6085	C1	-4	4	1163.75598	43.42
4822	C1	-4	3	1164.27502	43.93
6113	C1	-4	4	1164.53516	44.19
6045	C1	-4	4	1164.57922	44.24
6037	C1	-4	4	1164.83796	44.50
6301	C1	-4	3	1164.95262	44.61
6129	C1	-4	4	1165.23132	44.89
6076	C1	-4	4	1165.30584	44.97
6029	C1	-4	3	1165.39365	45.05
6139	C1	-4	4	1165.60923	45.27
5602	C1	-4	4	1165.64797	45.31
6086	C2	-4	4	1165.92193	45.58
6093	Cs	-4	4	1165.99532	45.65
5847	C1	-4	4	1166.23754	45.90
6231	C1	-4	4	1166.29027	45.95
6121	C1	-4	4	1166.99517	46.65
6145	C1	-4	3	1167.00875	46.67
5603	C1	-4	4	1167.08544	46.75
6063	C1	-4	3	1167.19094	46.85
6270	C1	-4	2	1167.1974	46.86
6087	C1	-4	4	1167.20384	46.86
5817	C1	-4	4	1167.29203	46.95
6162	C1	-4	3	1167.33881	47.00
6105	C1	-4	4	1167.76242	47.42
6038	C2	-4	4	1167.84954	47.51
6150	C1	-4	3	1167.94006	47.60
6122	C1	-4	4	1168.00232	47.66
5833	C1	-4	4	1168.09131	47.75
5587	C1	-4	4	1168.20421	47.86
6136	D2	-4	4	1168.47985	48.14
6040	Cs	-4	4	1168.76372	48.42
5621	C1	-4	4	1168.84288	48.50
5644	C1	-4	4	1168.84696	48.51
6232	C1	-4	3	1168.98581	48.65
6271	C2	-4	3	1169.00976	48.67
6192	C1	-4	3	1169.02326	48.68
5278	C1	-4	4	1169.04077	48.70
6153	C1	-4	3	1169.10954	48.77
6044	C1	-4	4	1169.1544	48.81
6144	C1	-4	4	1169.16489	48.82
6174	C1	-4	3	1169.17748	48.84
6230	C1	-4	3	1169.30981	48.97
6078	C1	-4	4	1169.36235	49.02
5140	C2	-4	4	1169.69295	49.35

6111	C1	-4	4	1170.26073	49.92

[a] PA means the number of pentagon adjacencies.

II. Fullerene anions further optimized at B3LYP/6-31G(d) level of theory.

Those di- and tetra- anions of C_{68} isomers with their relative energy less than 40 kcal/mol at AM1 level of theory were further optimized by DFT calculation at B3LYP/6-31G(d) level.

Table S3. DFT optimizations of C_{68}^{2-} isomers.

Spiral Number	Symmetry	Charge	PA	Relative Energy (kcal/mol)	HOMO (A.U.)	LUMO (A.U.)	Gap (eV)
6094	Cs	-2	2	0.0	0.03209	0.10892	2.09
6073	C2v	-2	2	7.6	0.03426	0.08725	1.44
6195	C2	-2	2	9.0	0.03836	0.10746	1.88
6146	C2	-2	2	9.0	0.03746	0.09514	1.57
6198	C1	-2	2	13.3	0.04171	0.10951	1.84
6148	C1	-2	2	14.5	0.04177	0.09742	1.51
6328	C2	-2	2	15.2	0.05184	0.10624	1.48
6149	C2	-2	2	22.2	0.04332	0.09747	1.47
6079	C1	-2	3	24.3	0.03485	0.08583	1.39
6101	C1	-2	3	25.3	0.03292	0.08836	1.51
6128	C1	-2	3	25.6	0.03829	0.09259	1.48
6075	C1	-2	3	25.6	0.03186	0.09034	1.59
6232	C1	-2	3	26.5	0.03915	0.10537	1.80
6309	C1	-2	3	26.5	0.04856	0.09302	1.21
6102	C1	-2	3	27.6	0.03496	0.08490	1.36
6097	C1	-2	3	27.7	0.03585	0.10077	1.77
6228	C1	-2	3	27.8	0.04626	0.09326	1.28
6050	C1	-2	3	28.0	0.03982	0.09499	1.50
6174	C1	-2	3	28.2	0.03365	0.10331	1.90
6088	C1	-2	3	30.0	0.03956	0.08868	1.34
6290	C2	-2	2	30.3	0.06312	0.09336	0.82
6319	C1	-2	3	30.5	0.04731	0.10573	1.59
6072	Cs	-2	3	30.7	0.03131	0.08030	1.33
6160	C1	-2	3	31.5	0.04159	0.09398	1.43
6070	C1	-2	3	31.6	0.03794	0.08662	1.32
6089	C2	-2	3	31.9	0.03843	0.08980	1.40
6201	C1	-2	3	32.0	0.03862	0.09629	1.57
6192	C1	-2	3	32.4	0.03552	0.09949	1.74
6116	C1	-2	3	32.5	0.04274	0.07547	0.89
6118	C2	-2	3	32.6	0.03940	0.07389	0.94

6147	C1	-2	3	32.9	0.03963	0.09478	1.50
6029	C1	-2	3	33.1	0.04051	0.09658	1.53
5205	C1	-2	3	33.4	0.04242	0.10744	1.77
6127	C1	-2	3	33.6	0.03834	0.09144	1.44
6193	C2	-2	3	33.6	0.03637	0.09269	1.53
6039	C1	-2	3	33.7	0.03499	0.07653	1.13
6117	C1	-2	3	33.8	0.04974	0.08310	0.91
5615	C1	-2	3	33.8	0.03833	0.09046	1.42
6230	C1	-2	3	34.0	0.04640	0.10099	1.49
6154	C1	-2	3	36.0	0.04303	0.09204	1.33
6138	C1	-2	3	36.3	0.04124	0.08231	1.12
6270	C1	-2	2	36.5	0.06056	0.09470	0.93
6150	C1	-2	3	37.3	0.04040	0.09575	1.51
6140	D3	-2	3	38.4	0.03734	0.06720	0.81
5596	C1	-2	3	41.1	0.03936	0.08224	1.17
6081	Cs	-2	4	51.0	0.02959	0.06633	1.00

Table S4. DFT optimizations of C_{68}^{4-} isomers.

Spiral Number	Symmetry	Charge	PA	Relative Energy (kcal/mol)	HOMO (A.U.)	LUMO (A.U.)	Gap (eV)
6073	*C2v*	-4	2	0.0	0.27659	0.32199	1.24
6140	*D3*	-4	3	8.1	0.26043	0.31417	1.46
6118	*C2*	-4	3	10.2	0.26633	0.32311	1.55
6116	*C1*	-4	3	11.2	0.26660	0.32991	1.72
6146	*C2*	-4	2	12.0	0.28540	0.32383	1.05
6039	*C1*	-4	3	13.4	0.26714	0.32856	1.67
6079	*C1*	-4	3	15.0	0.27538	0.33138	1.52
6072	*Cs*	-4	3	16.0	0.27225	0.32418	1.41
6102	*C1*	-4	3	17.0	0.27417	0.31625	1.15
6081	*Cs*	-4	4	18.9	0.25857	0.32132	1.71
6148	*C1*	-4	2	19.2	0.28581	0.32595	1.09
6101	*C1*	-4	3	19.4	0.27805	0.33038	1.42
6094	*Cs*	-4	2	20.1	0.29891	0.32985	0.84
6080	*C1*	-4	4	21.0	0.25531	0.32899	2.00
6117	*C1*	-4	3	21.9	0.27385	0.32930	1.51
6075	*C1*	-4	3	22.6	0.28062	0.32880	1.31
6138	*C1*	-4	3	22.9	0.27201	0.31670	1.22
6070	*C1*	-4	3	24.1	0.27718	0.32569	1.32
6110	*C1*	-4	3	25.0	0.27247	0.31651	1.20
6128	*C1*	-4	3	25.0	0.28216	0.32735	1.23
6088	*C1*	-4	3	25.4	0.27969	0.32851	1.33
6309	*C1*	-4	3	25.9	0.28190	0.33211	1.37
6195	*C2*	-4	2	26.3	0.29590	0.32882	0.90
6107	*C1*	-4	4	26.9	0.26178	0.32514	1.72

6099	*D2*	-4	4	27.0	0.26252	0.32367	1.66
6104	*C1*	-4	4	27.1	0.26941	0.32162	1.42
6089	*C2*	-4	3	27.5	0.27870	0.31316	0.94
6041	*C1*	-4	4	28.3	0.26773	0.31757	1.36
6149	*C2*	-4	2	28.4	0.28835	0.32276	0.94
6290	*C2*	-4	2	28.5	0.28052	0.32244	1.14
6228	*C1*	-4	3	28.6	0.28358	0.33074	1.28
6050	*C1*	-4	3	30.3	0.28436	0.32573	1.13
5615	*C1*	-4	3	31.3	0.28117	0.32359	1.15
6328	*C2*	-4	2	31.5	0.29548	0.33082	0.96
6127	*C1*	-4	3	31.7	0.28122	0.32371	1.16
5626	*Cs*	-4	4	32.3	0.26658	0.31746	1.38
6060	*C1*	-4	4	32.5	0.27362	0.31807	1.21
6108	*C2*	-4	3	33.0	0.27677	0.32635	1.35
6193	*C2*	-4	3	33.0	0.28191	0.32354	1.13
5596	*C1*	-4	3	34.2	0.27430	0.32491	1.38
6147	*C1*	-4	3	34.6	0.28353	0.31736	0.92
6198	*C1*	-4	2	34.7	0.29998	0.32677	0.73
5087	*Cs*	-4	4	34.7	0.26985	0.32843	1.59

III. The first step of $Sc_2S@C_{68}$ optimizations.

The number of formal electron transfer should be certain first because different numbers of formal charge transfer lead to different relative energy orders. Thus The optimization process of $Sc_2S@C_{68}$ was divided into two steps. In the first step, 16 isomers were chosen to encapsulate Sc_2S cluster in terms of the Table S3 and S4 with +2 and +3 formal valence states of a Sc atom, respectively. When a Sc atom is in +3 formal valence state, it is obvious that each of them possess 18 electrons (closed-shell). Consequently, only spin-restricted algorithms were applied. As for +2 formal valence state of each Sc atoms, both of them have one unpaired electron. Those two electrons may be ferromagnetically coupled (triplet, high-spin state) and non-ferromagnetically coupled (singlet, low-spin state). When high-spin or low-spin states were deal, spin-unrestricted algorithms and spin-unrestricted-singlet algorithms with always mixing HOMO & LUMO were employed respectively. The results of first-step optimization of $Sc_2@C_{68}$ isomers are listed in the Table S5. Clearly, either relative energies or HOMO/SOMO-LUMO gaps of "Closed-shell" and "Low-spin" state have no differences. As a result, those two states can be merged. Because relative energies of "Closed-shell" state are much lower than those of "High-spin" state, a formal four-electron transfer from intracluster to C_{68} cage seems reasonable.

Table S5. Relative energies and HOMO/SOMO-LUMO gaps of 16 isomers selected for the first step optimization.

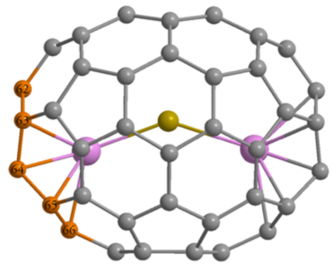
Spiral Number	Cage Symmetry	PA	Electronic State	Relative Energy (kcal/mol)	HOMO/SOMO (A.U.)	LUMO (A.U.)	Gap (eV)
6073	*C2v*	2	Low-spin	0.0	-0.18919	-0.13280	1.53
6073	*C2v*	2	Closed-shell	0.0	-0.18919	-0.13280	1.53

6073	*C2v*	2	High-spin	14.6	-0.16733	-0.15702	0.28
6146	*C2*	2	Low-spin	17.8	-0.17533	-0.12928	1.25
6146	*C2*	2	Closed-shell	17.8	-0.17533	-0.12928	1.25
6140	*D3*	3	Low-spin	21.6	-0.19438	-0.14700	1.29
6140	*D3*	3	Closed-shell	21.6	-0.19438	-0.14700	1.29
6039	*C1*	3	Low-spin	22.6	-0.19340	-0.13139	1.69
6039	*C1*	3	Closed-shell	22.6	-0.19339	-0.13140	1.69
6079	*C1*	3	Low-spin	23.0	-0.18873	-0.12544	1.72
6079	*C1*	3	Closed-shell	23.0	-0.18873	-0.12544	1.72
6116	*C1*	3	Low-spin	23.8	-0.18090	-0.12922	1.41
6116	*C1*	3	Closed-shell	23.8	-0.18090	-0.12922	1.41
6118	*C2*	3	Closed-shell	25.3	-0.18147	-0.13977	1.13
6118	*C2*	3	Low-spin	25.3	-0.18147	-0.13977	1.13
6148	*C1*	2	Low-spin	25.3	-0.16868	-0.12878	1.09
6148	*C1*	2	Closed-shell	25.3	-0.16868	-0.12879	1.09
6146	*C2*	2	High-spin	25.7	-0.16351	-0.14277	0.56
6102	*C1*	3	Low-spin	28.7	-0.18472	-0.14115	1.19
6102	*C1*	3	Closed-shell	28.7	-0.18472	-0.14115	1.19
6140	*D3*	3	High-spin	29.2	-0.18096	-0.15725	0.65
6094	*Cs*	2	Low-spin	29.6	-0.16976	-0.11559	1.47
6094	*Cs*	2	Closed-shell	29.6	-0.16976	-0.11559	1.47
6148	*C1*	2	High-spin	29.7	-0.16210	-0.13616	0.71
6118	*C2*	3	High-spin	30.9	-0.17131	-0.14772	0.64
6072	*Cs*	3	Low-spin	31.1	-0.18440	-0.13710	1.29
6072	*Cs*	3	Closed-shell	31.1	-0.18440	-0.13710	1.29
6101	*C1*	3	Low-spin	31.3	-0.17757	-0.12602	1.40
6101	*C1*	3	Closed-shell	31.3	-0.17757	-0.12602	1.40
6195	*C2*	2	Low-spin	31.6	-0.16475	-0.12853	0.99
6195	*C2*	2	Closed-shell	31.6	-0.16475	-0.12853	0.99
6195	*C2*	2	High-spin	32.6	-0.16208	-0.12863	0.91
6116	*C1*	3	High-spin	34.2	-0.16363	-0.14512	0.50
6102	*C1*	3	High-spin	35.6	-0.17344	-0.15140	0.60
6081	*Cs*	4	Closed-shell	39.2	-0.19195	-0.14338	1.32
6081	*Cs*	4	Low-spin	39.3	-0.19199	-0.14331	1.32
6072	*Cs*	3	High-spin	40.0	-0.16972	-0.15044	0.52
6039	*C1*	3	High-spin	40.0	-0.16517	-0.15744	0.21
6079	*C1*	3	High-spin	42.1	-0.15953	-0.15643	0.08
6094	*Cs*	2	High-spin	42.2	-0.15045	-0.13552	0.41
6101	*C1*	3	High-spin	43.1	-0.15890	-0.14528	0.37
6198	*C1*	2	Closed-shell	46.4	-0.17048	-0.13071	1.08
6198	*C1*	2	Low-spin	46.4	-0.17051	-0.13070	1.08
6198	*C1*	2	High-spin	48.1	-0.16753	-0.13555	0.87
6081	*Cs*	4	High-spin	49.2	-0.17374	-0.15711	0.45
6328	*C2*	2	Closed-shell	50.2	-0.17572	-0.12826	1.29

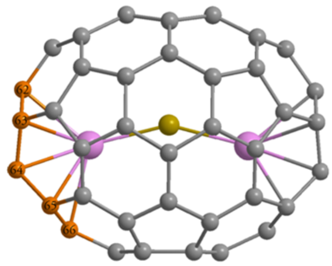
6328	*C2*	2	Low-spin	50.2	-0.17571	-0.12825	1.29
6328	*C2*	2	High-spin	59.9	-0.16261	-0.13992	0.62

IV. The second step of $Sc_2S@C_{68}$ optimization.

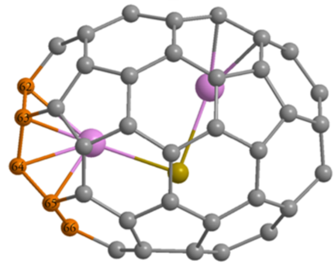
In this step, at least three more arrangements of a sulfide cluster in the carbon cages with top-six lowest relative energies were considered. Because we have anambiguously confirmed that "Low-spin" and "Closed-shell" states of each isomers are the same, and "High-spin" state of each isomers is less-stable, only "Closed-shell" state was taken into account in this part. The initial and optimized structures of them are depicted in the Figure S1 to Figure S6 repectively with relative energies.



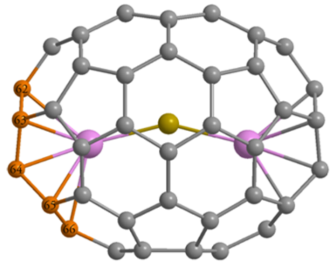
Isomer 1_Pristine



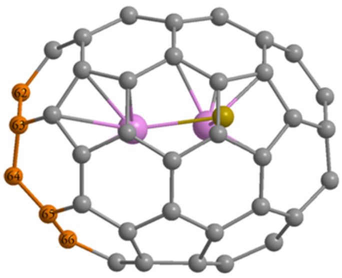
Isomer 1_Optimized (0.03 kcal/mol)



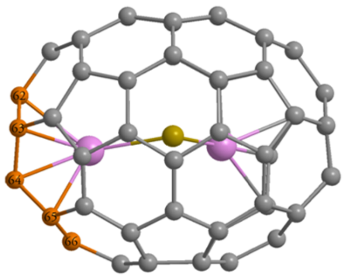
Isomer 2_Pristine



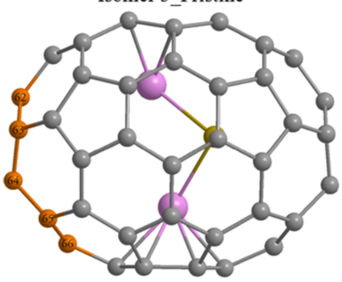
Isomer 2_Optimized (0.05 kcal/mol)



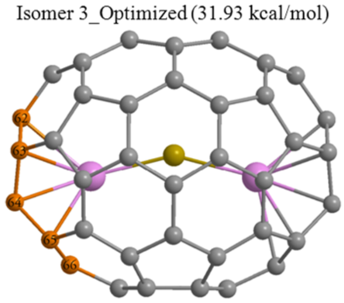
Isomer 3_Pristine



Isomer 3_Optimized (31.93 kcal/mol)



Isomer 4_Pristine



Isomer 4_Optimized (0.00 kcal/mol)

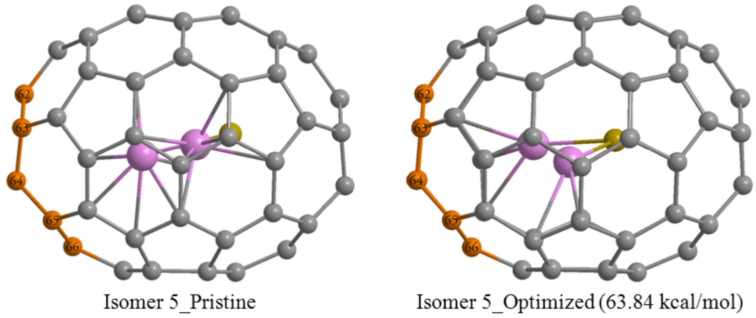


Figure S1. C_{2v}(6073)-C_{68} based isomers.

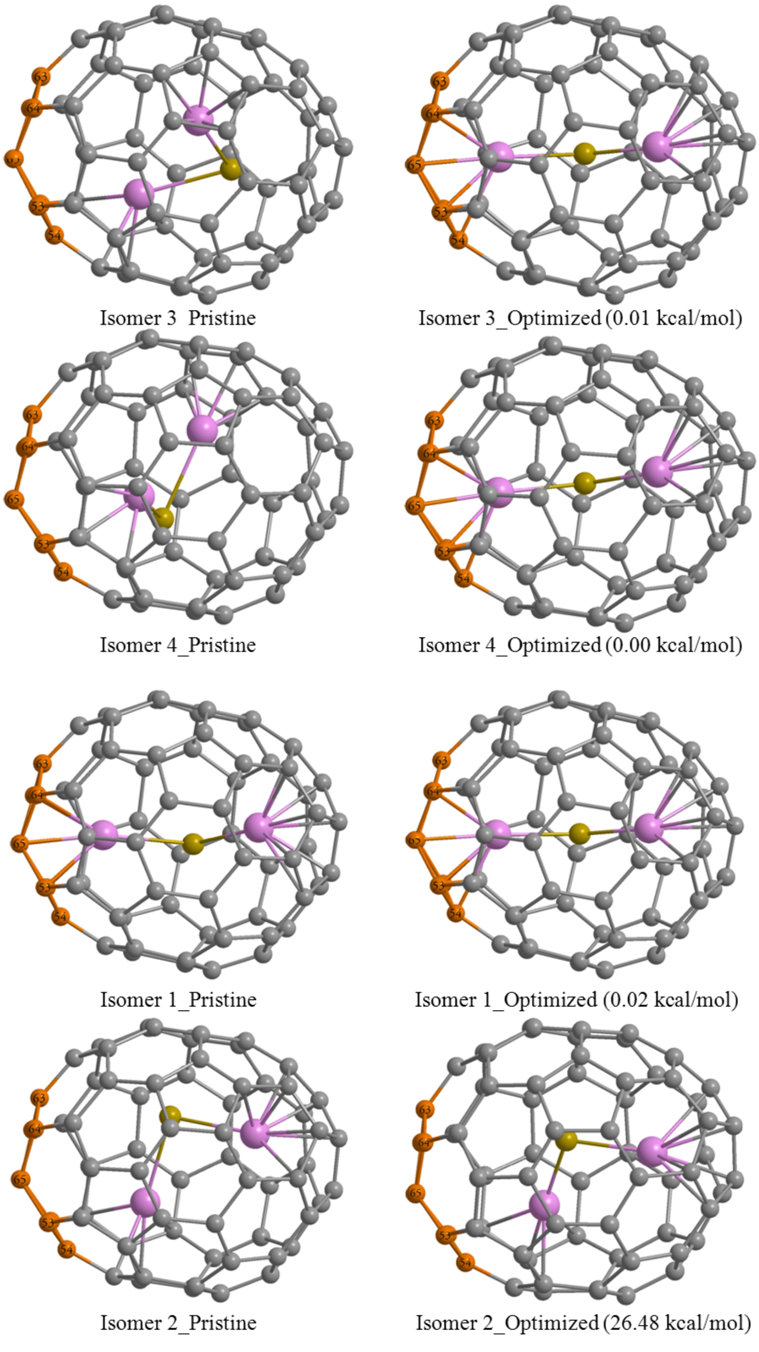
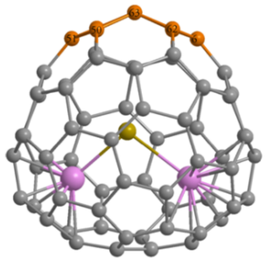
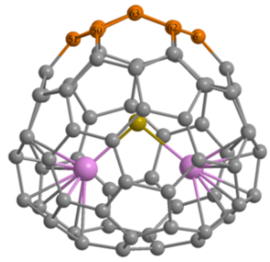


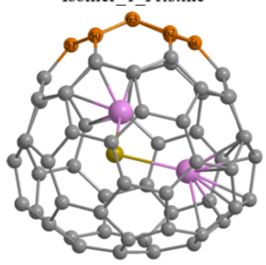
Figure S2. C_2(6146)-C_{68} based isomers.



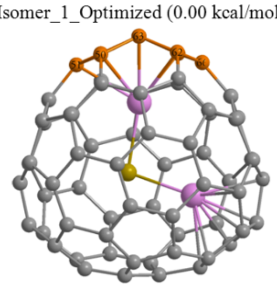
Isomer_1_Pristine



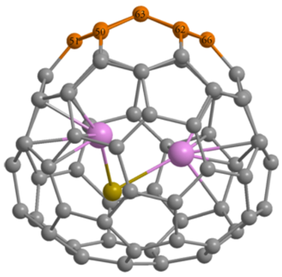
Isomer_1_Optimized (0.00 kcal/mol)



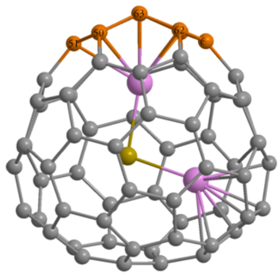
Isomer_2_Pristine



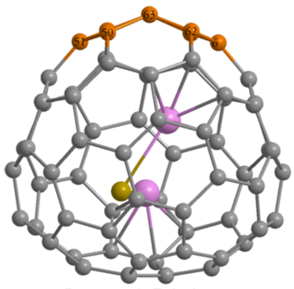
Isomer_2_Optimized (0.05 kcal/mol)



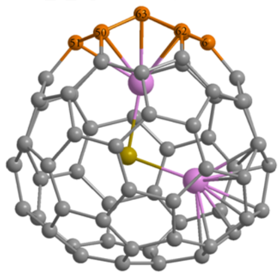
Isomer_3_Pristine



Isomer_3_Optimized (0.03 kcal/mol)

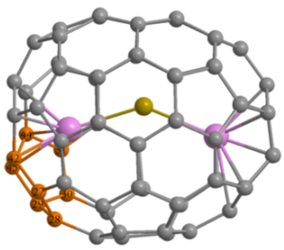


Isomer_4_Pristine

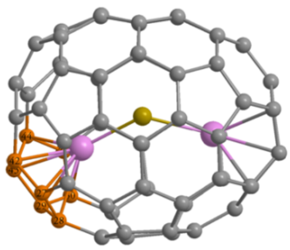


Isomer_2_Optimized (0.04 kcal/mol)

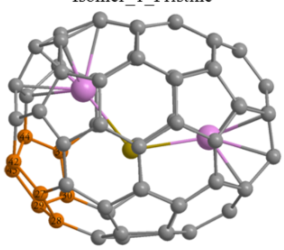
Figure S3. D_3(6140)-C_{68} based isomers.



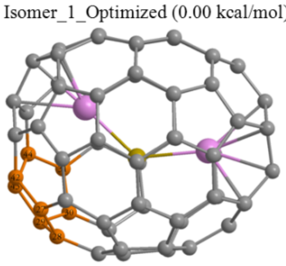
Isomer_1_Pristine



Isomer_1_Optimized (0.00 kcal/mol)



Isomer_2_Pristine



Isomer_1_Optimized (5.25 kcal/mol)

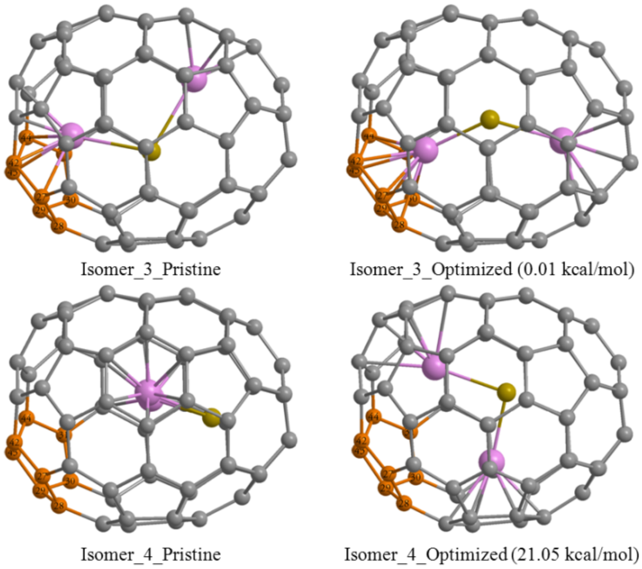


Figure S4. C_1(6039)-C_{68} based isomers.

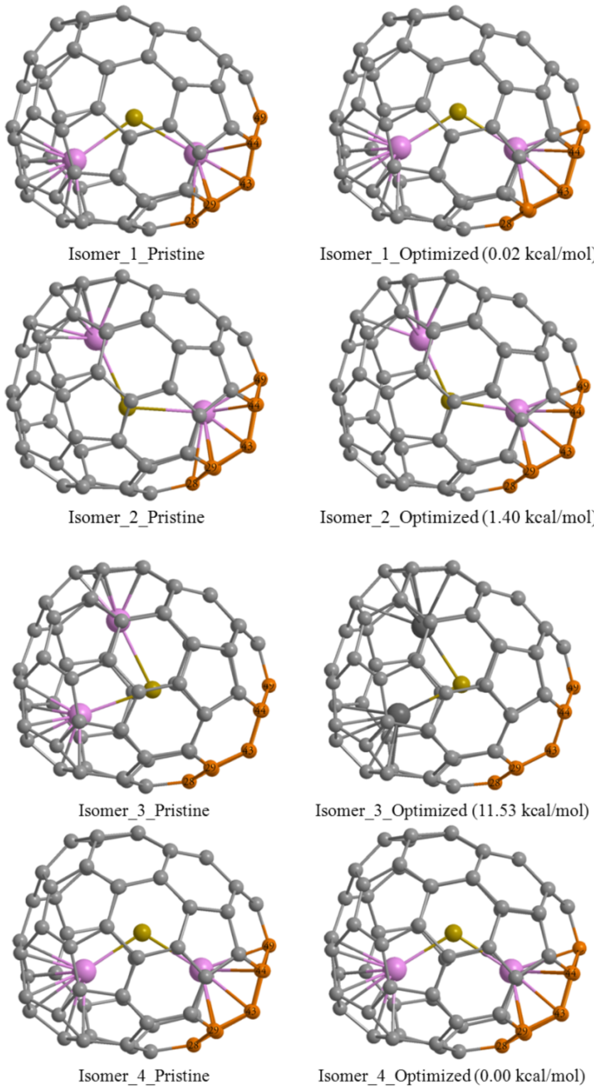
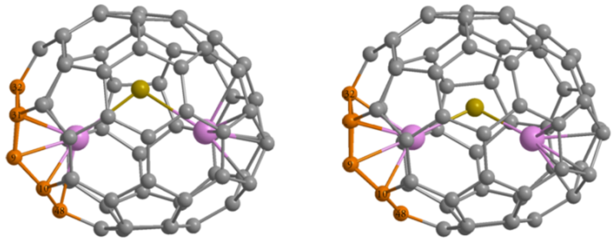
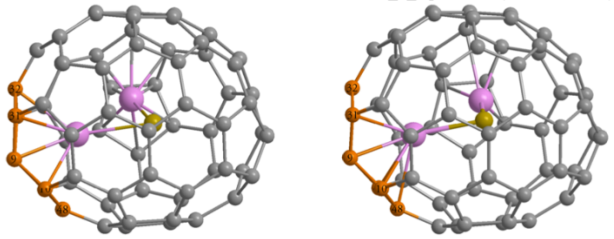


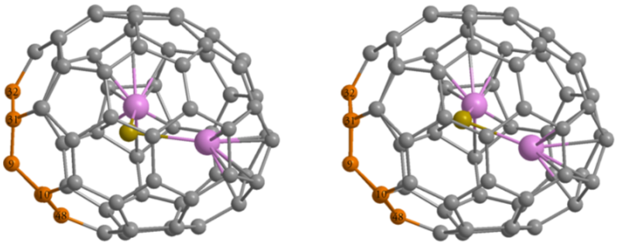
Figure S5. C_1(6079)-C_{68} based isomers.



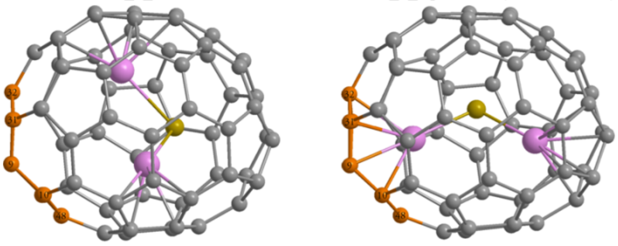
Isomer_1_Pristine Isomer_1_Optimized (0.77 kcal/mol)



Isomer_2_Pristine Isomer_2_Optimized (6.76 kcal/mol)

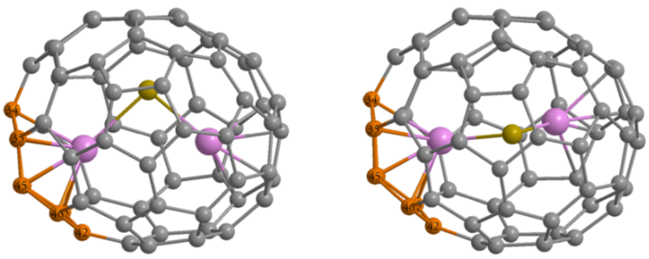


Isomer_3_Pristine Isomer_3_Optimized (0.00 kcal/mol)

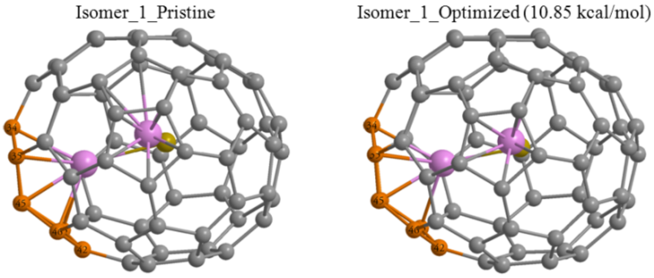


Isomer_4_Pristine Isomer_4_Optimized (0.74 kcal/mol)

Figure S6. C_1(6116)-C_{68} based isomers.



Isomer_1_Pristine Isomer_1_Optimized (10.85 kcal/mol)



Isomer_2_Pristine Isomer_2_Optimized (0.00 kcal/mol)

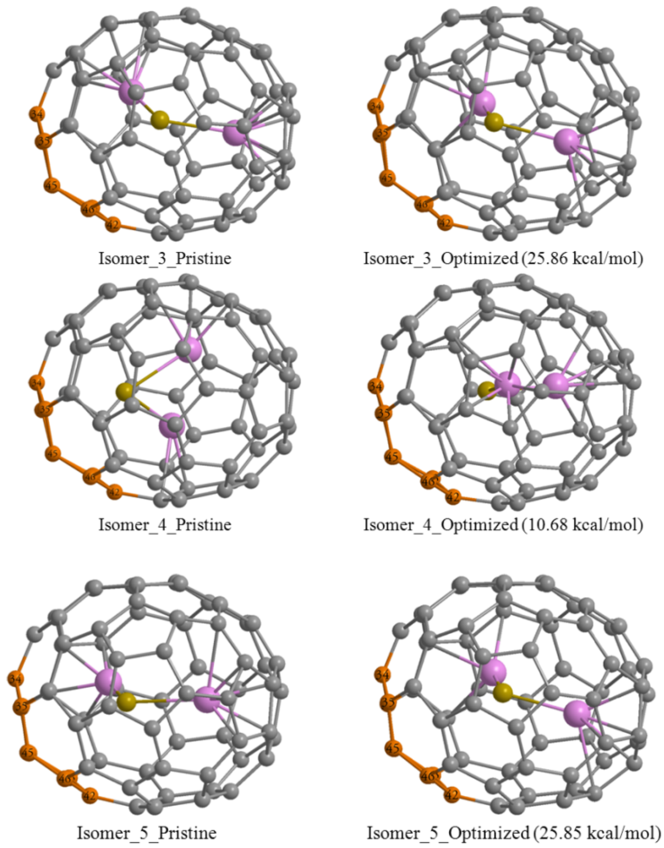
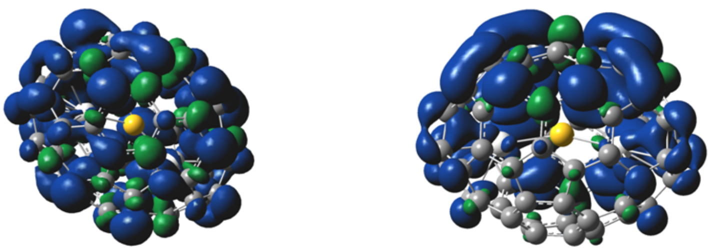


Figure S7. C_2(6328)-C_{68} based isomers.

V. Spin density of the oxidized cation and reduced anion of $Sc_2S@C_{2v}$(6073)-C_{68}

To further confirm above predictions, spin densities of the oxidized and reduced $Sc_2S@C_{68}$_C_{2v}(6073)-C_{68} also have been visualized. As shown in Figure S8, it is found that the spin density distribution of $[Sc_2S@C_{68}$_$C_{2v}(6073)$-$C_{68}]^+$ is akin to the HOMO distribution of the neutral molecule, which is mainly localized on the carbon cage. Similarly, the spin density distribution of $[Sc_2S@C_{68}$_$C_{2v}(6073)$-$C_{68}]^-$ is analogous to the LUMO distribution of the neutral molecule. As a consequence, it is no doubt that redox reactions mainly take place on the fullerene cage.



(*a*) (*b*)

Figure S8. Spin densities of the (*a*) oxidized $[Sc_2S@C_{68}$_$C_{2v}(6073)$-$C_{68}]^+$ cation and reduced (*b*) $[Sc_2S@C_{68}$_$C_{2v}(6073)$-$C_{68}]^-$ anion.

VI. Relationship between Sc-C bond lengths and Mayer bond orders.

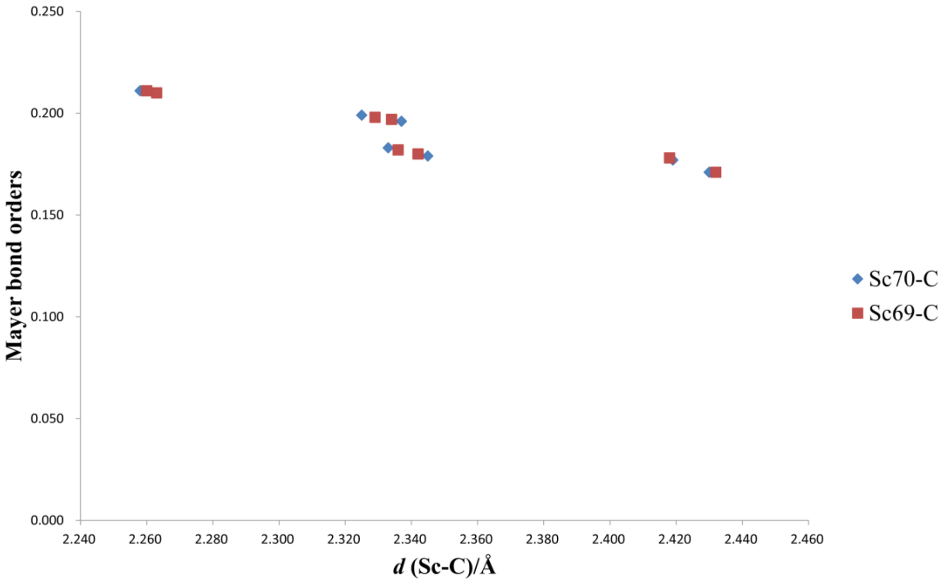


Figure S9. Correlation between Sc-C distances and Mayer bond order values in $Sc_2S@C_{2v}(6073)-C_{68}$.

VII. A brief introduction to BCP indicators derived from Bader's QTAIM.

Bader postulated that the presence of BCP between two atoms is an essential criterion for a bond existing between them.[1,2] Kobayashi *et al.*[3,4] first applied the BCP indicators to investigate the bonding features of EMFs. Recently, a very extensive study on metal-cage and inner cluster bonding of four typical EMFs was emerged by Popov and Dunsch.[5] They proposed that the bonding of all types have a substantial covalent character. Nowadays, it is believed that analysis of the energy density appears more useful than the analysis of electron density and it's Laplacian. Bonding between atoms can be considered as covalent if the total energy density at BCP H_{BCP} is negative.[6] Meanwhile, Espinosa et al.[7] suggest that the $|V_{BCP}|/G_{BCP}$ ratio (V_{BCP} and G_{BCP} means potential energy density and kinetic energy density respectively) at BCP should be an effective indicator classify different types of interactions: the ratio less than 1 means an ionic bond, a hydrogen bonds, or a van der Waals interaction; larger than 2 represent a covalent bond between the two atoms; and if the ratio is between 1 and 2, interactions between those two atoms were defined as "intermediate".

References

1 R. F. W. Bader, *Atoms in Molecules—A Quantum Theory*, Oxford University Press, Oxford, 1990.
2 R. F. W. Bader, *J. Phys. Chem. A,* 1998, **102,** 7314.
3 K. Kobayashi and S. Nagase, *Chem. Phys. Lett.,* 1999, **302,** 312.
4 K. Kobayashi and S. Nagase, *Chem. Phys. Lett.,* 2002, **362,** 373.
5 A. A. Popov and L. Dunsch, *Chem.–Eur. J.,* 2009, **15,** 9707.
6 D. Cremer, and E. Kraka, *Angew. Chem.,* 1984, **96,** 612; *Angew. Chem. Int. Ed. Engl.,* 1984, **23,** 627.
7 E. Espinosa, I. Alkorta, J. Elguero, and E. Molins, *J. Chem. Phys.,* 2002, **117,** 5529.

VIII. Theoretical ^{13}C NMR chemical shifts of $Sc_2S@C_{2v}$(6073)-C_{68}.

Through the gauge-independent atomic orbital method, the ^{13}C NMR chemical shifts were evaluated at the B3LYP/6-31G(d)-Lanl2dz level of theory. Theoretical chemical shift values have been calibrated to the observed C_{60} line (143.15 ppm). The ^{13}C NMR chemical shifts are depicted in Table S6, respectively.

Table S6. Computed ^{13}C NMR chemical shifts of $Sc_2S@C_{2v}$(6073)-C_{68}.

Chemical Shifts ppm	Intensity	Chemical Shifts ppm	Intensity	Chemical Shifts ppm	Intensity
156.62	4	145.94	4	148.85	2
152.76	4	143.49	4	147.13	2
148.31	4	142.16	4	144.10	2
148.12	4	142.01	4	143.37	2
147.65	4	139.73	4	141.11	2
147.43	4	134.57	4	140.88	2
146.62	4	152.97	2	140.21	2

IX. UV-vis-NIR absorption bands of $Sc_2S@C_{2v}$(6073)-C_{68}.

Table S2. Computed electronic excitation energies, oscillator strengths and assignments of the most intense low-energy excitations in the UV-vis-NIR absorption spectrum of $Sc_2S@C_{2v}$(6073)-C_{68}.

Band (nm)	Wavelength (nm)	Energy (eV)	f^a	Leading Configurations[b](%)
1323	1323.6	0.94	0.0029	HOMO→LUMO(99)
967	966.9	1.28	0.0074	HOMO-1→LUMO(99)
723	722.9	1.72	0.0506	HOMO→LUMO+1(90)
613	612.7	2.02	0.0130	HOMO-3→LUMO(87)
509	512.0	2.42	0.0176	HOMO→LUMO+4(79)
	511.3	2.43	0.0130	HOMO-6→LUMO(87)
	495.8	2.50	0.0036	HOMO-3→LUMO+1(86)
	477.5	2.60	0.0102	HOMO-4→LUMO+1(57)
	475.7	2.61	0.0034	HOMO-9→LUMO(92)
	456.3	2.72	0.0036	HOMO-2→LUMO+4(76)
414	432.2	2.87	0.0053	HOMO→LUMO+6(40) HOMO→LUMO+7(22)
	414.7	2.99	0.0166	HOMO-11→LUMO(54)
	414.3	2.99	0.0033	HOMO-4→LUMO+2(29) HOMO-1→LUMO+5(51)

[a] Only excitations with *f* (oscillator strength) > 0.0015 are listed. [b]Contributions of less than 10% are omitted.

X. Cartesian coordinates of $Sc_2S@C_{2v}$(6073)-C_{68}

C -0.02553100 -0.00499500 0.12764200

C	1.37455200	-0.00238800	0.11065600
C	2.11131300	1.23481600	0.10347400
C	3.24332800	1.05294900	-0.77353100
C	3.76874300	2.13944100	-1.52891900
C	4.21582700	1.87999400	-2.86874800
C	4.07598700	2.87139900	-3.89533300
C	3.69461600	2.18901400	-5.11916800
C	2.73751300	2.77653100	-5.99894000
C	1.73974300	1.93602000	-6.57519800
C	0.36348300	2.38993300	-6.66424600
C	-0.48471500	1.27037200	-6.37552100
C	-1.67630500	1.43357600	-5.59070000
C	-2.07050400	0.36512900	-4.73707600
C	-2.62774800	0.62081900	-3.43059300
C	-2.23106200	-0.47008900	-2.57760200
C	-1.86681200	-0.24377000	-1.24478100
C	-0.76140200	-0.95868100	-0.66108900
C	-0.72797100	1.27619400	0.10862700
C	-1.86933800	1.12845000	-0.74134500
C	-2.34644400	2.21182700	-1.53209700
C	-2.73906200	1.95029800	-2.93486200
C	-2.59814500	3.00266100	-3.88217100
C	-2.04165000	2.74961300	-5.18974100
C	-1.26906400	3.89577800	-5.60858100
C	-0.01972000	3.71754800	-6.31419900
C	1.04468100	4.67159600	-6.03972300
C	2.38221000	4.16285200	-5.76293300
C	2.92565600	4.91819000	-4.64034200
C	3.62920700	4.19132900	-3.59344100
C	3.26756900	4.48359400	-2.22399500
C	3.27210000	3.43886400	-1.22520700
C	2.14051300	3.61742700	-0.34691400
C	1.45272800	2.49337600	0.19071300
C	-0.02662500	2.51198800	0.19555700
C	-0.70052200	3.64640000	-0.33906000
C	-1.84128100	3.49847600	-1.19042800
C	-1.80863900	4.59020800	-2.16190400
C	-2.17324000	4.32045000	-3.48650300
C	-1.40173200	4.90419900	-4.57872000
C	-0.38238000	5.85921800	-4.33140000
C	0.81737000	5.80799500	-5.16704600
C	1.97194400	5.96115500	-4.30843000
C	1.49509900	6.10690000	-2.93160400
C	2.16200600	5.36755000	-1.92011200

C	1.43175500	4.78795300	-0.79707300
C	0.03226000	4.82838800	-0.78860500
C	-0.68449500	5.44356800	-1.87540100
C	0.03397800	6.07634500	-2.94797500
C	2.08629200	-0.96907400	-0.71845000
C	3.21179500	-0.28469200	-1.31888300
C	3.57197200	-0.52148100	-2.69893600
C	4.04851000	0.58472100	-3.46141300
C	3.67669500	0.77985800	-4.85129600
C	2.70265800	-0.06684900	-5.45920100
C	1.72304600	0.52672800	-6.30875900
C	0.33603800	0.10298300	-6.23206900
C	-0.07549300	-0.99512500	-5.42122100
C	-1.32468000	-0.87193800	-4.70314000
C	-1.47758400	-1.43151000	-3.37684000
C	-0.48075900	-2.25535100	-2.79291400
C	-0.06283400	-1.95659900	-1.42473100
C	1.39685200	-2.00959500	-1.39305900
C	1.86997000	-2.38974000	-2.72429500
C	2.84523200	-1.56300600	-3.41011600
C	2.31643300	-1.26224800	-4.73470100
C	0.96708500	-1.80882800	-4.81319800
C	0.71665500	-2.54132300	-3.58510600
Sc	0.88502600	-0.36931500	-2.98370900
Sc	0.95694000	4.00925500	-3.80025000
S	0.56455800	1.90905500	-2.94912900