Supplementary Material

Vibrational and electronic spectroscopy of neutral antimony coordination compounds of the 1,3-dithiole-2-thione-4,5-dithiolate (dmit)

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Table 1S. Main singlet transition energies (eV) and the oscillator strength from the ground state of [SbL(dmit)] (L= Br or I), with the B3LYP method.

SbBr(dmit)				SbI(dmit)			
State	**Dominant configuration**	**Wavelength (nm)**	**Oscillator strength**	**State**	**Dominant configuration**	**Wavelength (nm)**	**Oscillator strength**
A"	HOMO→LUMO (96%)	546	0.0002	A"	HOMO→L+1 (96%)	560	0.0001
A'	HOMO→L+1 (79%)	444	0.0096	A'	HOMO→LUMO (88%)	513	0.0420
A'	H-1→LUMO (60%) HOMO→L+2 (37%)	413	0.0001	A"	H-1→LUMO (90%)	419	0.0000
A"	H-1→L+2 (41%) H-1→L+3 (53%)	412	0.0000	A'	H-1→L+1 (43%) HOMO→L+2 (54%)	418	0.0011
A'	HOMO→L+2 (25%) HOMO→L+3 (37%)	396	0.0326	A"	H-1→L+2 (24%) H-1→L+3 (62%)	411	0.0000
A"	H-1→L+1 (98%)	358	0.0000	A'	H-1→L+1 (34%) HOMO→L+2 (23%) HOMO→L+3 (34%)	407	0.0286
A'	HOMO→L+2 (19%) HOMO→L+3 (41%)	348	0.2383	A'	H-2→LUMO (91%)	380	0.0035
A"	H-2→LUMO (95%)	337	0.0000	A"	H-4→LUMO (80%) H-2→L+1 (13%)	370	0.0003
A'	HOMO→L+4 (95%)	330	0.0041	A"	H-2→L+1 (84%)	363	0.0020
A"	H-1→L+2 (56%) H-1→L+3 (42%)	327	0.0001	A'	H-4→L+1 (64%) H-3→LUMO (34%)	352	0.0036
A'	H-3→LUMO (93%)	318	0.0228	A"	H-3→L+1 (94%)	351	0.0005
A"	H-4→LUMO (89%)	301	0.0045	A'	H-1→L+1 (15%) HOMO→L+3 (48%)	349	0.2612
A'	H-2→L+1 (79%)	297	0.0086	A'	HOMO→L+4 (85%)	331	0.0049
A"	H-3→L+1 (79%)	288	0.0001	A"	H-1→L+2 (72%) H-1→L+3 (27%)	329	0.0001
A"	H-1→L+4 (94%)	284	0.0016	A'	H-5→L+1 (16%) H-4→L+1 (18%) H-3→LUMO (32%)	325	0.0457
A'	H-4→L+1 (82%)	279	0.0203	A"	H-5→LUMO (89%)	308	0.0006
A'	H-2→L+2 (51%) H-2→L+3 (20%)	278	0.0008	A'	H-5→L+1 (74%)	308	0.0080
A"	H-3→L+2 (38%) HOMO→L+5 (50%)	275	0.0074	A'	H-3→L+2 (46%) H-2→L+2 (30%)	289	0.0039
A'	H-5→LUMO (55%) H-4→L+2 (18%)	269	0.0140	A"	H-4→L+2 (80%) H-4→L+3 (17%)	287	0.0006
A"	H-5→L+1 (17%) H-3→L+2 (20%) H-3→L+3 (30%)	266	0.0127	A"	H-1→L+4 (94%)	285	0.0016
A"	H-5→L+1 (75%)	260	0.0000	A"	HOMO→L+5 (64%)	276	0.0083
A'	H-2→L+2 (19%) H-2→L+3 (50%) H-1→L+5 (18%)	260	0.0713	A'	H-3→L+2 (21%) H-2→L+2 (31%)	275	0.1034
A'	H-1→L+5 (78%)	250	0.0975	A'	H-2→L+3 (82%)	269	0.0023
A"	H-3→L+2 (20%) H-3→L+3 (50%)	249	0.0250	A'	H-3→L+3 (60%)	264	0.1081
A'	HOMO→L+6 (89%)	247	0.0063	A"	H-6→L+1 (70%)	264	0.0025
A'	H-6→LUMO (42%) H-4→L+2 (28%)	243	0.0424	A"	H-4→L+3 (55%)	262	0.0035
A"	HOMO→L+7 (75%)	240	0.0000	A"	H-6→L+1 (17%) H-5→L+2 (29%) H-5→L+3 (22%)	257	0.0171
A"	H-7→LUMO (72%)	239	0.0204	A'	H-1→L+5 (91%)	252	0.0367
A'	H-6→LUMO (21%) H-4→L+2 (39%) H-4→L+3 (33%)	237	0.0286	A'	HOMO→L+6 (72%)	248	0.0256

A'	H-4→L+3 (17%) H-2→L+4 (53%)	235	0.0116	A'	H-6→LUMO (42%) HOMO→L+6 (17%)	245	0.1042
A'	H-6→LUMO (19%) H-4→L+3 (31%) H-2→L+4 (33%)	235	0.0621	A"	H-5→L+3 (51%) HOMO→L+7 (16%)	244	0.0241
A"	H-5→L+2 (51%) H-5→L+3 (22%)	234	0.0167	A"	H-7→LUMO (66%)	242	0.0039
A'	HOMO→L+8 (87%)	229	0.0163	A"	H-7→LUMO (24%) HOMO→L+7 (60%)	239	0.0053
A"	H-3→L+4 (84%)	227	0.0001	A'	H-3→L+4 (84%)	238	0.0070
A"	H-6→L+1 (91%)	223	0.0003	A'	H-7→L+1 (83%)	238	0.0111
A"	H-5→L+2 (28%) H-5→L+3 (69%)	220	0.0019	A"	H-5→L+4 (40%) H-4→L+4 (50%)	229	0.0002
A'	H-8→LUMO (20%) H-7→L+1 (55%)	217	0.0823	A'	HOMO→L+8 (92%)	227	0.0126
A"	H-2→L+5 (29%) H-1→L+6 (64%)	217	0.0002	A'	H-2→L+4 (96%)	226	0.0000
A"	H-2→L+5 (47%) H-1→L+6 (28%)	215	0.0100	A'	H-8→L+1 (19%) H-6→L+2 (56%)	224	0.0217
A'	H-1→L+7 (92%)	214	0.0011	A"	H-8→LUMO (44%) H-3→L+5 (50%)	222	0.0009

Table 2S. Main singlet transition energies (eV) and the oscillator strength from the ground state of [SbBr(dmit)], with the B3LYP-CPCM method.

MeCN				DMSO				THF				MeOH			
State	Dominant configuration	Waveleng. (nm)	Oscillator strength	State	Dominant configuration	Waveleng. (nm)	Oscillator strength	State	Dominant configuration	Waveleng. (nm)	Oscillator strength	State	Dominant configuration	Waveleng. (nm)	Oscillator strength
A"	HOMO→LUMO (96%)	459	0.0005	A"	HOMO→LUMO (96%)	458	0.0006	A"	HOMO→LUMO (96%)	470	0.0005	A"	HOMO→LUMO (96%)	459	0.0005
A'	HOMO→L+1 (25%) HOMO→L+2 (60%)	409	0.0177	A'	HOMO→L+1 (23%) HOMO→L+2 (62%)	409	0.0179	A'	HOMO→L+1 (78%)	414	0.0201	A'	HOMO→L+1 (28%) HOMO→L+2 (58%)	409	0.0179
A'	HOMO→L+1 (57%) HOMO→L+2 (26%)	392	0.1863	A'	HOMO→L+1 (60%) HOMO→L+2 (25%)	395	0.2110	A"	H-1→L+2 (80%)	392	0.0000	A'	HOMO→L+1 (54%) HOMO→L+2 (29%)	392	0.1830
A"	H-1→L+1 (81%)	387	0.0000	A"	H-1→L+1 (84%)	387	0.0000	A'	HOMO→L+2 (76%)	391	0.1765	A"	H-1→L+1 (78%) H-1→L+2 (19%)	387	0.0000
A'	HOMO->L+3 (86%)	360	0.0092	A'	HOMO->L+3 (87%)	360	0.0108	A'	HOMO→L+3 (85%)	366	0.0068	A'	HOMO→L+3 (86%)	360	0.0088
A'	HOMO->L+4 (93%)	321	0.0076	A'	HOMO→L+4 (95%)	322	0.0049	A'	H-1→LUMO (87%)	329	0.1911	A'	HOMO→L+4 (92%)	321	0.0085
A'	H-1->LUMO (85%)	319	0.1424	A'	H-1→LUMO (88%)	319	0.1559	A'	HOMO→L+4 (96%)	323	0.0041	A'	H-1→LUMO (84%)	319	0.1399
A"	H-1→L+2 (82%)	305	0.0000	A"	H-1→L+2 (85%)	304	0.0000	A"	H-1→L+1 (82%)	313	0.0000	A"	H-1→L+2 (79%)	305	0.0000
A"	H-2→LUMO (93%)	297	0.0006	A"	H-2→LUMO (93%)	296	0.0007	A"	H-2→LUMO (94%)	302	0.0004	A"	H-2→LUMO (93%)	297	0.0006
A'	H-3→LUMO (93%)	292	0.0389	A'	H-3→LUMO (93%)	292	0.0424	A'	H-3→LUMO (94%)	295	0.0376	A'	H-3→LUMO (93%)	292	0.0382
A"	H-4→LUMO (48%) H-3→L+1 (20%)	279	0.0050	A"	H-4→LUMO (56%) HOMO→L+5 (18%)	280	0.0065	A"	H-1→L+3 (87%)	284	0.0001	A"	H-4→LUMO (41%) H-3→L+1 (24%)	279	0.0043
A"	H-3→L+2 (60%)	278	0.0001	A"	H-3→L+2 (67%)	278	0.0000	A"	H-4→LUMO (76%)	282	0.0063	A"	H-3→L+2 (59%) HOMO→L+5 (18%)	278	0.0004
A'	H-2→L+1 (34%) H-2→L+2 (52%)	278	0.0253	A'	H-2→L+1 (35%) H-2→L+2 (52%)	278	0.0304	A'	H-2→L+1 (82%)	281	0.0222	A'	H-2→L+1 (37%) H-2→+2 (50%)	278	0.0246
A"	H-4→LUMO (21%) H-1→L+3 (52%)	277	0.0006	A"	H-4→LUMO (19%) H-1→L+3 (50%)	277	0.0003	A"	H-3→L+1 (52%) H-3→L+2 (23%)	279	0.0000	A"	H-4→LUMO (24%) H-1→L+3 (54%)	277	0.0007
A"	H-3→L+1 (47%) H-1→L+3 (25%)	272	0.0004	A"	H-3→L+1 (43%) H-1→L+3 (34%)	272	0.0004	A"	H-3→L+1 (23%) H-3→L+2 (33%)	273	0.0012	A"	H-3→L+1 (46%) H-1→L+3 (24%)	272	0.0005
A'	H-2→L+1 (52%) H-2→L+2 (32%)	270	0.1932	A'	H-2→L+1 (52%) H-2→L+2 (32%)	272	0.1985	A'	H-4→L+1 (22%) H-2→L+2 (56%)	270	0.2023	A'	H-2→L+1 (49%) H-2→L+2 (34%)	270	0.1926
A'	H-4→L+1 (18%) H-4→L+2 (68%)	267	0.0333	A'	H-4→L+1 (15%) H-4→L+2 (71%)	268	0.0361	A'	H-4→L+1 (55%) H-2→L+2 (24%)	269	0.0110	A'	H-4→L+1 (21%) H-4→L+2 (65%)	267	0.0324
A"	H-1→L+4 (66%) HOMO→L+5 (18%)	261	0.0419	A"	H-1→L+4 (64%) HOMO→L+5 (20%)	261	0.0511	A"	H-1→L+4 (78%)	265	0.0290	A"	H-1→L+4 (66%) HOMO→L+5 (18%)	261	0.0413
A"	H-3→L+3 (30%) H-1→L+4 (22%)	255	0.0219	A"	H-3→L+3 (23%) H-1→L+4 (25%)	255	0.0328	A'	H-2→L+3 (80%)	258	0.0171	A"	H-3→L+3 (31%) H-1→L+4 (22%)	255	0.0200
A'	H-2→L+3 (79%)	254	0.0134	A'	H-2→L+3 (79%)	254	0.0141	A"	H-3→L+2 (19%) H-3→L+3 (42%) H-3→L+2 (18%)	256	0.0212	A'	H-2→L+3 (80%)	254	0.0136
A"	H-3→L+3 (48%) HOMO→L+5 (16%)	251	0.0609	A"	H-3→L+3 (54%) HOMO→L+5 (13%)	251	0.0636	A"	H-3→L+3 (35%) HOMO→L+5 (20%)	253	0.0807	A"	H-3→L+3 (47%) HOMO→L+5 (16%)	251	0.0609
A'	H-4→L+1 (69%) H-4→L+2 (18%)	250	0.0130	A'	H-4→L+1 (74%) H-4→L+2 (15%)	251	0.0135	A'	H-5→LUMO (56%) H-4→L+3 (24%)	251	0.0049	A'	H-4→L+1 (65%) H-4→L+2 (21%)	250	0.0128
A'	H-5→LUMO (51%) H-4→L+3 (26%)	247	0.0110	A'	H-5→LUMO (52%) H-4→L+3 (26%)	247	0.0123	A"	H-5→L+1 (72%)	249	0.0036	A'	H-5→LUMO (51%) H-4→L+3 (26%)	247	0.0111

A"	H-5→L+2 (71%)	247	0.0055	A"	H-5→L+2 (73%)	247	0.0047	A'	H-4→L+2 (76%)	247	0.0224	A"	H-5→L+1 (19%) H-5→L+2 (69%)	247	0.0058
A'	HOMO→L+6 (38%) HOMO→L+7 (47%)	236	0.0051	A'	HOMO→L+6 (38%) HOMO→L+7 (45%)	236	0.0075	A'	HOMO→L+6 (84%)	238	0.0047	A'	HOMO→L+6 (37%) HOMO→L+7 (48%)	236	0.0046
A"	H-3→L+4 (22%) HOMO→L+8 (68%)	234	0.0022	A"	H-3→L+4 (23%) HOMO→L+8 (67%)	234	0.0025	A"	H-3→L+4 (17%) HOMO→L+8 (73%)	235	0.0022	A"	H-3→L+4 (21%) HOMO→L+8 (68%)	234	0.0022
A'	H-2→L+4 (47%) HOMO→L+7 (35%)	232	0.0082	A'	H-4→L+3 (20%) H-2→L+4 (25%) HOMO→L+7 (25%)	232	0.0792	A'	H-4→L+3 (22%) H-1→L+5 (52%)	234	0.1750	A'	H-2→L+4 (46%) HOMO→L+7 (35%)	232	0.0073
A'	H-6→LUMO (15%) H-4→L+3 (36%)	231	0.1925	A'	H-4→L+3 (22%) H-2→L+4 (29%)	232	0.1576	A'	H-4→L+3 (21%) H-1→L+5 (33%)	233	0.0537	A'	H-6→LUMO (16%) H-4→L+3 (36%)	231	0.1857
A'	H-1→L+5 (79%)	230	0.0219	A'	H-1→L+5 (79%)	230	0.0259	A'	H-2→L+4 (47%) HOMO→L+7 (32%)	232	0.0065	A'	H-1→L+5 (78%)	230	0.0210
A'	H-2→L+4 (33%) HOMO→L+6 (43%)	228	0.0222	A'	H-2→L+4 (29%) H-1→L+5 (14%) HOMO→L+6 (44%)	228	0.0267	A"	H-7→LUMO (91%)	230	0.0291	A'	H-2→L+4 (35%) HOMO→L+6 (41%)	228	0.0224
A"	H-7→LUMO (87%)	228	0.0209	A"	H-7→LUMO (88%)	228	0.0241	A'	H-2→L+4 (27%) HOMO→L+7 (61%)	229	0.0154	A"	H-7→LUMO (87%)	227	0.0203
A"	H-3→L+4 (62%) HOMO→L+8 (20%)	227	0.0001	A"	H-3→L+4 (60%) HOMO→L+8 (20%)	227	0.0001	A"	H-3→L+4 (72%)	227	0.0002	A"	H-3→L+4 (62%) HOMO→L+8 (19%)	227	0.0000
A"	H-5→L+1 (66%)	226	0.0094	A"	H-5→L+1 (68%)	226	0.0107	A'	H-6→LUMO (75%)	225	0.1440	A"	H-5→L+1 (64%)	226	0.0092
A'	H-6→LUMO (75%)	223	0.1460	A'	H-6→LUMO (79%)	223	0.1501	A"	H-5→L+2 (72%)	225	0.0106	A'	H-6→LUMO (74%)	223	0.1458
A"	H-6→L+1 (22%) H-5→L+3 (57%) H-6→L+1 (30%)	219	0.0008	A"	H-6→L+1 (21%) H-5→L+3 (59%) H-6→L+1 (31%)	219	0.0011	A"	H-5→L+3 (74%)	221	0.0045	A"	H-6→L+1 (28%) H-5→L+3 (50%) H-6→L+1 (25%)	219	0.0005
A"	H-6→L+2 (42%) H-5→L+3 (21%)	218	0.0028	A"	H-6→L+2 (42%) H-5→L+3 (20%)	218	0.0047	A"	H-6→L+1 (88%)	219	0.0001	A"	H-6→L+2 (39%) H-5→L+3 (28%)	218	0.0025
A'	H-7→L+1 (16%) H-7→L+2 (56%)	216	0.1360	A'	H-7→L+1 (14%) H-7→L+2 (60%)	217	0.1463	A'	H-7→L+1 (65%)	217	0.1505	A'	H-7→L+1 (19%) H-7→L+2 (53%)	216	0.1340
A"	H-6→L+1 (32%) H-6→L+2 (47%)	214	0.0606	A"	H-6→L+1 (33%) H-6→L+2 (48%)	215	0.0702	A"	H-6→L+2 (70%)	214	0.0548	A"	H-6→L+1 (31%) H-6→L+2 (48%)	214	0.0596
A'	HOMO→L+9 (91%)	212	0.0417	A'	HOMO→L+9 (91%)	212	0.0419	A'	HOMO→L+9 (91%)	211	0.0369	A'	HOMO→L+9 (91%)	212	0.0421
A"	H-2→L+5 (79%)	210	0.0014	A"	H-2→L+5 (81%)	210	0.0022	A"	H-2→L+5 (67%)	211	0.0000	A"	H-2→L+5 (79%)	210	0.0014

Table 3S. Main singlet transition energies (eV) and the oscillator strength from the ground state of [SbI(dmit)], with the B3LYP-CPCM method.

MeCN				DMSO				THF				MeOH			
State	**Dominant configuration**	**Waveleng. (nm)**	**Oscillator strength**	**State**	**Dominant configuration**	**Waveleng. (nm)**	**Oscillator strength**	**State**	**Dominant configuration**	**Waveleng. (nm)**	**Oscillator strength**	**State**	**Dominant configuration**	**Waveleng. (nm)**	**Oscillator strength**
A'	HOMO→LUMO (90%)	477	0.0957	A'	HOMO→LUMO (91%)	478	0.1065	A'	HOMO→LUMO (90%)	484	0.0949	A'	HOMO→LUMO (90%)	477	0.0944
A"	HOMO→L+1 (96%)	472	0.0005	A"	HOMO→L+1 (96%)	472	0.0006	A"	HOMO→L+1 (96%)	484	0.0005	A"	HOMO→L+1 (96%)	472	0.0005
A'	HOMO→L+2 (81%)	393	0.1522	A'	HOMO→L+2 (83%)	395	0.1719	A'	HOMO→L+2 (76%)	392	0.1392	A'	HOMO→L+2 (81%)	393	0.1498
A"	H-1→L+2 (95%)	387	0.0000	A"	H-1→L+2 (95%)	387	0.0000	A"	H-1→L+2 (95%)	392	0.0000	A"	H-1→L+2 (95%)	387	0.0000
A'	HOMO→L+3 (91%)	373	0.0011	A'	HOMO→L+3 (92%)	373	0.0019	A'	HOMO→L+3 (88%)	378	0.0005	A'	HOMO→L+3 (91%)	373	0.0011
A"	H-1→LUMO (91%)	354	0.0000	A"	H-1→LUMO (89%)	353	0.0001	A"	H-1→LUMO (94%)	364	0.0000	A"	H-1→LUMO (91%)	354	0.0000
A'	H-3→LUMO (39%) H-2→LUMO (54%)	350	0.0082	A'	H-3→LUMO (37%) H-2→LUMO (56%)	351	0.0096	A'	H-3→LUMO (36%) H-2→LUMO (57%)	355	0.0071	A'	H-3→LUMO (39%) H-2→LUMO (54%)	350	0.0079
A"	H-4→LUMO (84%)	341	0.0013	A"	H-4→LUMO (83%)	341	0.0013	A"	H-4→LUMO (87%)	346	0.0012	A"	H-4→LUMO (84%)	341	0.0013
A'	H-1→L+1 (87%)	324	0.1901	A'	H-1→L+1 (87%)	324	0.2023	A'	H-1→L+1 (86%)	334	0.2455	A'	H-1→L+1 (86%)	324	0.1869
A'	HOMO→L+4 (77%)	322	0.0080	A'	HOMO→L+4 (81%)	322	0.0095	A'	H-4→L+1 (23%) H-3→LUMO (38%) H-2→LUMO (23%)	325	0.0239	A'	HOMO→L+4 (74%)	321	0.0084
A'	H-4→L+1 (23%) H-3→LUMO (32%) H-2→LUMO (22%)	320	0.0295	A'	H-4→L+1 (22%) H-3→LUMO (37%) H-2→LUMO (23%)	320	0.0372	A"	H-3→L+1 (20%) H-2→L+1 (74%)	324	0.0054	A'	H-4→L+1 (22%) H-3→LUMO (31%) H-2→LUMO (21%) HOMO→L+4 (21%)	320	0.0280
A"	H-2→L+1 (76%)	317	0.0053	A"	H-2→L+1 (78%)	318	0.0063	A'	HOMO→L+4 (85%)	323	0.0054	A"	H-3→L+1 (18%) H-2→L+1 (75%)	317	0.0052
A"	H-3→L+1 (78%)	310	0.0001	A"	H-3→L+1 (80%)	310	0.0001	A"	H-3→L+1 (76%)	316	0.0003	A"	H-3→L+1 (77%)	310	0.0001
A'	H-4→L+1 (64%)	303	0.0793	A'	H-4→L+1 (66%)	304	0.0868	A'	H-4→L+1 (59%)	308	0.0870	A'	H-4→L+1 (64%)	303	0.0783
A"	H-5→LUMO (83%)	301	0.0030	A"	H-5→LUMO (83%)	301	0.0036	A"	H-5→LUMO (86%)	302	0.0027	A"	H-5→LUMO (83%)	301	0.0030
A'	H-5→L+1 (80%)	284	0.0100	A'	H-5→L+1 (81%)	284	0.0113	A'	H-5→L+1 (83%)	288	0.0104	A'	H-5→L+1 (80%)	284	0.0099
A"	H-1→L+3 (83%)	281	0.0002	A"	H-1→L+3 (79%)	280	0.0003	A"	H-1→L+3 (95%)	288	0.0000	A"	H-1→L+3 (83%)	281	0.0002
A'	H-2→L+2 (83%)	277	0.1118	A'	H-2→L+2 (75%)	278	0.1415	A'	H-2→L+2 (75%)	276	0.1341	A'	H-2→L+2 (84%)	277	0.1067
A"	H-4→L+2 (48%) HOMO→L+5 (18%)	275	0.0001	A"	H-4→L+2 (46%) H-1→L+3 (17%) HOMO→L+5 (17%)	276	0.0002	A"	H-5→L+2 (18%) H-4→L+2 (43%) HOMO→L+5 (26%)	275	0.0000	A"	H-5→L+2 (15%) H-4→L+2 (48%) HOMO→L+5 (18%)	275	0.0002
A'	H-3→L+2 (86%)	272	0.1086	A'	H-3→L+2 (80%)	273	0.0849	A'	H-3→L+2 (72%)	272	0.0720	A'	H-3→L+2 (86%)	272	0.1129
A"	H-4→L+3 (63%) HOMO→L+5 (16%)	265	0.0109	A"	H-4→L+3 (55%) HOMO→L+5 (20%)	266	0.0167	A"	H-4→L+3 (80%)	268	0.0066	A"	H-4→L+3 (64%) HOMO→L+5 (15%)	265	0.0100
A'	H-3→L+3 (88%)	264	0.0034	A'	H-3→L+3 (87%)	264	0.0017	A'	H-3→L+3 (85%)	267	0.0137	A'	H-3→L+3 (88%)	264	0.0033
A"	H-4→L+2 (25%) H-4→L+3 (28%) HOMO→L+5 (26%)	263	0.0211	A"	H-4→L+2 (20%) H-4→L+3 (36%) HOMO→L+5 (23%)	263	0.0235	A"	H-1→L+4 (66%) HOMO→L+5 (19%)	265	0.0280	A"	H-4→L+2 (26%) H-4→L+3 (27%) HOMO→L+5 (26%)	263	0.0199
A'	H-6→LUMO (26%) H-2→L+3 (60%)	261	0.0954	A'	H-6→LUMO (24%) H-2→L+3 (62%)	261	0.1095	A'	H-6→LUMO (21%) H-2→L+3 (63%)	264	0.1012	A'	H-6→LUMO (25%) H-2→L+3 (60%)	261	0.0936
A"		261	0.0099	A"	H-1→L+4 (72%)	261	0.0099	A"	H-4→L+2 (47%)	263	0.0059	A"	H-1→L+4 (75%)	261	0.0112

	H-1→L+4 (74%)								H-1→L+4 (19%) HOMO→L+5 (12%)						
A"	H-6→L+1 (46%) H-5→L+2 (34%)	253	0.0026	A"	H-6→L+1 (44%) H-5→L+2 (36%)	254	0.0037	A"	H-6→L+1 (68%) H-5→L+2 (17%)	255	0.0011	A"	H-6→L+1 (46%) H-5→L+2 (34%)	253	0.0026
A'	H-6→LUMO (49%) H-2→L+3 (16%)	250	0.2349	A'	H-6→LUMO (51%) H-2→L+3 (16%)	251	0.2654	A'	H-9→LUMO (13%) H-6→LUMO (55%)	251	0.2470	A'	H-9→LUMO (15%) H-6→LUMO (49%) H-2→L+3 (16%)	250	0.2303
A"	H-6→L+1 (29%) H-5→L+2 (21%) H-5→L+3 (27%)	250	0.0436	A"	H-6→L+1 (34%) H-5→L+2 (21%) H-5→L+3 (22%)	250	0.0563	A"	H-5→L+2 (43%) H-5→L+3 (31%)	250	0.0400	A"	H-6→L+1 (28%) H-5→L+2 (21%) H-5→L+3 (29%)	250	0.0411
A"	H-6→L+1 (14%) H-5→L+3 (58%)	245	0.0449	A"	H-5→L+3 (64%)	245	0.0457	A"	H-5→L+3 (50%)	247	0.0618	A"	H-6→L+1 (15%) H-5→L+3 (57%)	245	0.0451
A"	H-7→LUMO (88%)	239	0.0027	A"	H-7→LUMO (88%)	239	0.0028	A"	H-7→LUMO (87%)	239	0.0014	A"	H-7→LUMO (89%)	239	0.0026
A'	H-3→L+4 (14%) HOMO→L+6 (68%)	237	0.0007	A'	H-3→L+4 (18%) HOMO→L+6 (63%)	237	0.0009	A'	H-3→L+4 (13%) HOMO→L+6 (73%)	239	0.0007	A'	H-3→L+4 (14%) HOMO→L+6 (70%)	237	0.0006
A'	H-3→L+4 (34%) H-2→L+4 (31%) HOMO→L+6 (24%)	234	0.0055	A'	H-3→L+4 (32%) H-2→L+4 (28%) HOMO→L+6 (30%)	234	0.0062	A'	H-3→L+4 (33%) H-2→L+4 (24%) H-1→L+5 (24%)	235	0.0059	A'	H-3→L+4 (35%) H-2→L+4 (31%) HOMO→L+6 (23%)	234	0.0054
A"	H-5→L+4 (16%) HOMO→L+7 (60%)	233	0.0026	A"	H-5→L+4 (16%) HOMO→L+7 (58%)	234	0.0031	A"	H-5→L+4 (13%) HOMO→L+7 (65%)	234	0.0033	A"	H-5→L+4 (15%) HOMO→L+7 (61%)	233	0.0025
A'	H-1→L+5 (96%)	231	0.0280	A'	H-1→L+5 (96%)	230	0.0303	A'	H-1→L+5 (73%)	234	0.0310	A'	H-1→L+5 (96%)	230	0.0274
A"	H-5→L+4 (30%) H-4→L+4 (36%) HOMO→L+7 (30%)	227	0.0005	A"	H-5→L+4 (29%) H-4→L+4 (35%) HOMO→L+7 (32%)	227	0.0007	A"	H-5→L+4 (34%) H-4→L+4 (38%) HOMO→L+7 (24%)	227	0.0005	A"	H-5→L+4 (30%) H-4→L+4 (36%) HOMO→L+7 (30%)	227	0.0005
A'	H-7→L+1 (15%) H-6→L+2 (21%) HOMO→L+8 (58%)	226	0.0348	A'	H-6→L+2 (38%) HOMO→L+8 (44%)	226	0.0467	A'	H-7→L+1 (84%)	227	0.0264	A'	H-6→L+2 (17%) HOMO→L+8 (63%)	226	0.0309
A'	H-7→L+1 (19%) H-6→L+2 (39%) HOMO→L+8 (34%)	226	0.0415	A'	H-6→L+2 (41%) HOMO→L+8 (48%)	226	0.0342	A'	HOMO→L+8 (89%)	226	0.0111	A'	H-7→L+1 (25%) H-6→L+2 (39%) HOMO→L+8 (29%)	226	0.0439
A'	H-7→L+1 (52%) H-6→L+2 (34%)	225	0.0005	A'	H-7→L+1 (69%) H-6→L+2 (15%)	225	0.0021	A'	H-6→L+2 (89%)	223	0.0536	A'	H-7→L+1 (48%) H-6→L+2 (39%)	225	0.0013
A'	H-3→L+4 (44%) H-2→L+4 (53%)	220	0.0004	A'	H-3→L+4 (43%) H-2→L+4 (54%)	221	0.0004	A'	H-3→L+4 (40%) H-2→L+4 (58%)	221	0.0003	A'	H-3→L+4 (44%) H-2→L+4 (53%)	220	0.0004
A"	H-8→LUMO (68%)	219	0.0076	A"	H-8→LUMO (68%)	219	0.0091	A"	H-8→LUMO (64%) H-2→L+5 (14%)	220	0.0073	A"	H-8→LUMO (68%)	219	0.0076

Table 4S. Ionization potential (IP), transition energies, term values (TV), oscillator strengths, orbital size, character for selected transitions, and assignment for the S *1s* NEXAFS spectrum of [SbBr(dmit)].

Thione	IVO Calculation					Character (%)						Assignment
MO	**IP (eV)**	**Energy (eV)**	**TV (eV)**	**Oscillator strength**	**Size (Å)**	**% St**	**% Sb**	**% Br**	**s**	**p**	**d**	
(LUMO)	2470.997	2462.811	-8.186	0.0003210	2.587	11	2	9	1	98	1	$\pi^*_{Sm} + \pi^*_{S\text{-}C=S}$
(LUMO+1)	***2470.997***	***2465.711***	***-5.286***	***0.0011098***	***3.841***	***9***	***0***	***0***	***0***	***100***	***0***	$\boldsymbol{\pi^*_{C=S} + \pi^*_{Sa}}$
(LUMO+2)	2470.997	2468.373	-2.624	0.0002181	3.565	2	2	0	44	56	0	$\sigma^*_{Ce\text{-}S}$
(LUMO+3)	2470.997	2468.671	-2.326	0.0000149	2.470	0	4	0	9	91	0	$\pi^*_{C=C}$
(LUMO+4)	2470.997	2469.031	-1.966	0.0000055	2.930	3	46	3	29	70	0	$\sigma^*_{Sb\text{-}S} + \sigma^*_{Ce\text{-}S}$
(LUMO+5)	***2470.997***	***2469.540***	***-1.457***	***0.0012950***	***4.121***	***33***	***8***	***4***	***57***	***43***	***0***	$\boldsymbol{\sigma^*_{S\text{-}C=S}}$
(LUMO+6)	2470.997	2469.680	-1.317	0.0007429	3.818	34	20	10	47	52	1	$\sigma^*_{Sb\text{-}Br} + \sigma^*_{S\text{-}C=S}$
(LUMO+7)	2470.997	2470.497	-0.500	0.0001662	3.266	0	3	0	53	47	0	$\sigma^*_{Ce\text{-}S}$
(LUMO+8)	2470.997	2470.687	-0.310	0.0000559	3.889	2	1	0	35	64	0	$\sigma^*_{Ct\text{-}S}$
Thiolate												
(LUMO)	***2474.050***	***2469.036***	***-5.014***	***0.0008809***	***2.985***	***23***	***66***	***4***	***17***	***82***	***1***	$\boldsymbol{\sigma^*_{Sb\text{-}S}}$
(LUMO+1)	2474.050	2470.134	-3.916	0.0002952	3.172	5	60	34	17	81	2	$\sigma^*_{Sb\text{-}Br}$
(LUMO+2)	2474.050	2470.223	-3.827	0.0006383	2.827	32	54	4	28	70	1	$\sigma^*_{Sb\text{-}S}$
(LUMO+3)	2474.050	2471.537	-2.513	0.0000173	4.468	1	0	0	1	99	0	$\pi^*_{S\text{-}C=S}$
(LUMO+4)	***2474.050***	***2471.966***	***-2.084***	***0.0011903***	***2.580***	***48***	***4***	***0***	***37***	***62***	***1***	$\boldsymbol{\sigma^*_{Sm\text{-}Ce}}$
(LUMO+5)	2474.050	2472.264	-1.786	0.0007830	2.576	52	4	0	33	67	1	$\pi^*_{Sm\text{-}Ce} + \pi^*_{C=C}$
(LUMO+6)	2474.050	2473.208	-0.842	0.0001068	3.427	12	5	0	39	60	1	$\sigma^*_{Sa\text{-}Ce}$
(LUMO+7)	2474.050	2473.976	-0.074	0.0001557	2.973	84	5	0	58	41	1	$\sigma^*_{Sm\text{-}Ce}$
Thiole												
(LUMO)	2474.934	2470.64	-4.295	0.0005362	4.485	16	0	0	0	99	1	$\pi^*_{S\text{-}C=S}$
(LUMO+1)	2474.934	2471.26	-3.672	0.0002528	3.062	18	39	2	29	71	1	$\sigma^*_{Sb\text{-}S}$
(LUMO+2)	***2474.934***	***2471.89***	***-3.046***	***0.0028395***	***3.401***	***34***	***3***	***0***	***41***	***58***	***1***	$\boldsymbol{\sigma^*_{Sa\text{-}Ce}}$
(LUMO+3)	2474.934	2472.22	-2.710	0.0000098	3.240	2	59	31	17	81	1	$\sigma^*_{Sb\text{-}Br}$
(LUMO+4)	2474.934	2472.38	-2.553	0.0002399	2.967	10	51	5	32	68	0	$\sigma^*_{Sb\text{-}S}$
(LUMO+5)	2474.934	2472.96	-1.976	0.0001793	2.359	11	1	0	2	93	1	$\pi^*_{C=C}$
(LUMO+6)	***2474.934***	***2474.17***	***-0.765***	***0.0009415***	***3.341***	***21***	***3***	***0***	***62***	***37***	***1***	$\boldsymbol{\sigma^*_{Sa\text{-}Ce} + \sigma^*_{Sm\text{-}Ce}}$
(LUMO+7)	2474.934	2474.84	-0.093	0.0002849	3.189	14	5	0	53	47	1	$\sigma^*_{Sm\text{-}Ce} + \sigma^*_{Sa\text{-}Ce}$

[a] Italic data represent the orbitals involved in the transitions of larger intensity below the IP values.

[b] S_t = sulfur thione ,S_a = sulfur thiole, S_m = sulfur thiolate, Ce = carbon ethylenic, Ct = carbon of thione.

Table 5S. Ionization potential (IP), transition energies, term values (TV), oscillator strengths, orbital size, character for selected transitions, and assignment for the S *1s* NEXAFS spectrum of [SbI(dmit)].

Thione	IVO Calculation					Character (%)						Assignment
MO	**IP (eV)**	**Energy (eV)**	**TV (eV)**	**Oscillator strength**	**Size (Å)**	**% St**	**% Sb**	**% I**	**s**	**p**	**d**	
(LUMO)	2467.620	2458.147	-9.473	0.0000003	3.390	0	0	91	0	100	0	n*p* I
(LUMO+1)	***2467.620***	***2463.295***	***-4.325***	***0.0010221***	***4.140***	***9***	***0***	***0***	***0***	***100***	***0***	$\pi^*_{C=S}$
(LUMO+2)	2467.620	2465.505	-2.115	0.0000355	3.150	1	38	2	35	64	1	σ^*_{Sb-S}
(LUMO+3)	2467.620	2466.237	-1.383	0.0003374	3.805	1	9	0	54	46	0	σ^*_{Sa-C}
(LUMO+4)	2467.620	2466.588	-1.032	0.0000004	3.386	4	38	2	20	79	1	σ^*_{Sb-S}
(LUMO+5)	2467.620	2467.108	-0.512	0.0000068	2.567	0	1	0	5	95	0	$\pi^*_{C=C}$
(LUMO+6)	***2467.620***	***2467.602***	***-0.018***	***0.0017833***	***4.912***	***37***	***0***	***0***	***59***	***41***	***0***	$\sigma^*_{S-C=S}$
Thiolate												
(LUMO)	***2474.078***	***2468.96***	***-5.114***	***0.0008719***	***2.893***	***19***	***64***	***7***	***18***	***81***	***1***	σ^*_{Sb-S}
(LUMO+1)	2474.078	2469.52	-4.562	0.0002601	3.070	7	54	37	18	81	1	σ^*_{Sb-I}
(LUMO+2)	2474.078	2470.23	-3.850	0.0006112	2.826	30	55	3	23	75	2	σ^*_{Sb-S}
(LUMO+3)	2474.078	2471.57	-2.511	0.0000054	4.764	1	0	0	0	99	0	$\pi^*_{S-C=S}$
(LUMO+4)	***2474.078***	***2472.04***	***-2.036***	***0.0011439***	***2.708***	***35***	***4***	***0***	***38***	***61***	***1***	σ^*_{Sm-Ce}
(LUMO+5)	2474.078	2472.26	-1.815	0.0008325	2.713	33	4	0	32	67	1	$\pi^*_{Sm-Ce} + \pi^*_{C=C}$
(LUMO+6)	2474.078	2473.22	-0.863	0.0000914	3.632	3	4	0	39	60	1	σ^*_{Sa-Ce}
(LUMO+7)	2474.078	2474.03	-0.045	0.0001712	3.049	33	5	0	58	41	1	σ^*_{Sm-Ce}
Thiole												
(LUMO)	2474.949	2470.630	-4.319	0.0005493	4.751	16	0	0	0	99	1	$\pi^*_{S-C=S}$
(LUMO+1)	2474.949	2471.149	-3.800	0.0002333	3.008	17	38	2	29	70	1	σ^*_{Sb-S}
(LUMO+2)	2474.949	2471.545	-3.404	0.0000060	3.089	0	54	36	21	79	1	σ^*_{Sb-I}
(LUMO+3)	***2474.949***	***2471.862***	***-3.087***	***0.0028561***	***3.657***	***34***	***3***	***0***	***40***	***59***	***1***	σ^*_{Sa-Ce}
(LUMO+4)	2474.949	2472.295	-2.654	0.0002360	2.980	12	51	2	26	73	1	σ^*_{Sb-S}
(LUMO+5)	2474.949	2472.949	-2.000	0.0001547	2.558	10	1	0	4	95	1	$\pi^*_{C=C}$
(LUMO+6)	***2474.949***	***2474.134***	***-0.815***	***0.0009584***	***3.520***	***21***	***2***	***0***	***63***	***36***	***1***	$\sigma^*_{Sa-Ce} + \sigma^*_{Sm-Ce}$
(LUMO+7)	2474.949	2474.787	-0.162	0.0003049	3.269	14	4	0	52	47	1	$\sigma^*_{Sm-Ce} + \sigma^*_{Sa-Ce}$
(LUMO+8)	2474.949	2474.928	-0.021	0.0001490	3.688	34	2	0	40	60	0	$\sigma^*_{Sm-Ce} + \sigma^*_{Sa-Ce}$

[a] Italic data represent the orbitals involved in the transitions of larger intensity below the IP values.

[b] S_t = sulfur thione ,S_a = sulfur thiole, S_m = sulfur thiolate, Ce = carbon ethylenic, Ct = carbon of thione.

Table 6S. Deconvolution parameters for the XANES spectra for [SbL(dmit)] (L= Br or I).

Peak	Area	Center (eV)	Width (eV)	Height (a.u.)
		[SbBr(dmit)]		
G	7.402E-02	2468.11	1.7285	2.72616E-02
G	1.18	2470.74	2.9130	0.38057
E		2470.99	15.250	5.24198E-02
G	0.373	2473.52	2.5443	0.13788
E		2474.03	15.915	5.31591E-02
E		2474.91	21.103	9.20112E-02
G	0.443	2475.24	10.519	3.95848E-02
G	7.683E-02	2479.27	5.7006	1.26613E-02
G	0.330	2485.48	9.8403	3.15493E-02
		[SbI(dmit)]		
G	5.672E-02	2467.69	3.2733	1.62782E-02
E		2467.71	20.158	3.96649E-02
G	1.73	2470.91	3.0096	0.53982
G	0.551	2473.62	2.7492	0.18813
E		2474.00	35.188	0.16967
E		2474.97	21.120	4.81098E-02
G	0.587	2478.10	7.4734	7.38324E-02
G	0.444	2485.04	8.8583	4.71270E-02
G	0.271	2492.48	10.921	2.33256E-02

G = gaussian
E = error

Table 7S. Term Values of Core (TV_{XANES}) and Valence (TV_{UV-Vis}) for [SbL(dmit)] (L= Br or I).

IP (eV)	Peak (eV)	TV (eV)
	[SbBr(dmit)]	
6.24 (HOMO)	3.27 (380 nm)	-2.97
2470.99	2465.71	-5.28
2474.05	2471.53	-2.52
2474.93	2470.64	-4.29
2472.00	2468.3	-3.70
	[SbI(dmit)]	
6.32 (HOMO)	2.99 (415 nm)	-3.33
2467.62	2463.29	-4.33
2474.07	2471.57	-2.50
2474.94	2470.63	-4.31
2472.00	2469.30	-2.70

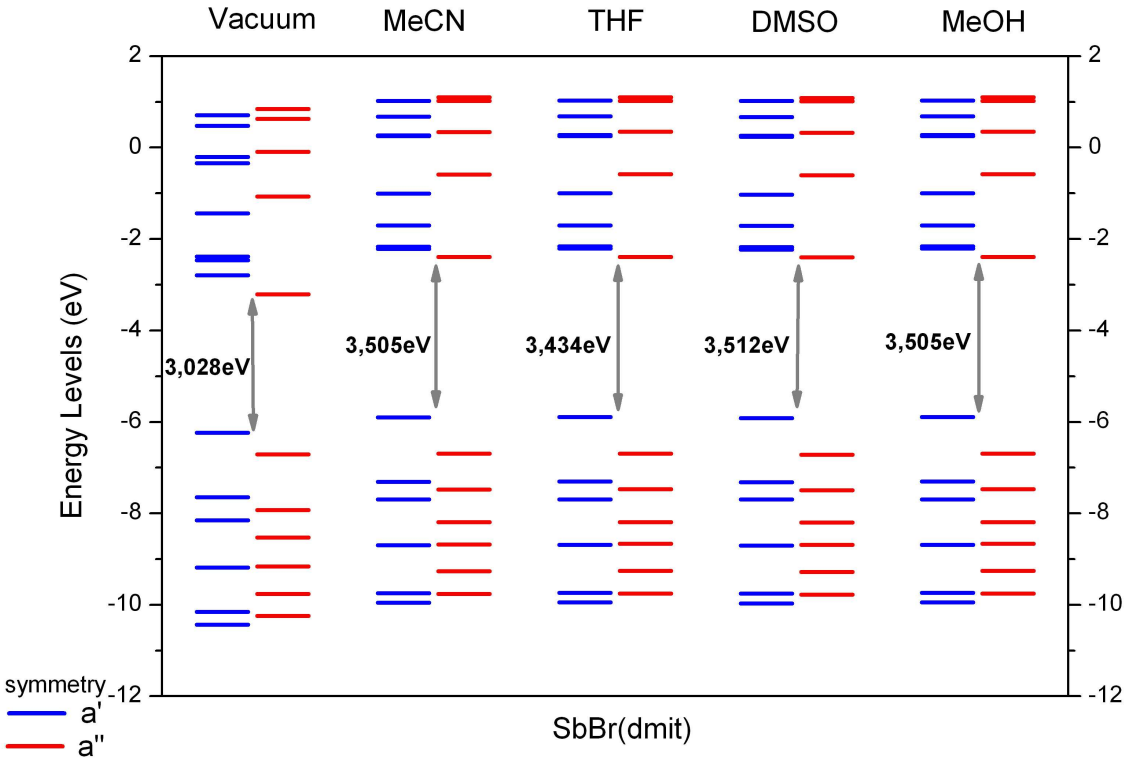

Figure 1S. Energy levels diagrams of [SbBr(dmit)], with SCF molecular orbitals within the B3LYP and B3LYP-CPCM methods.

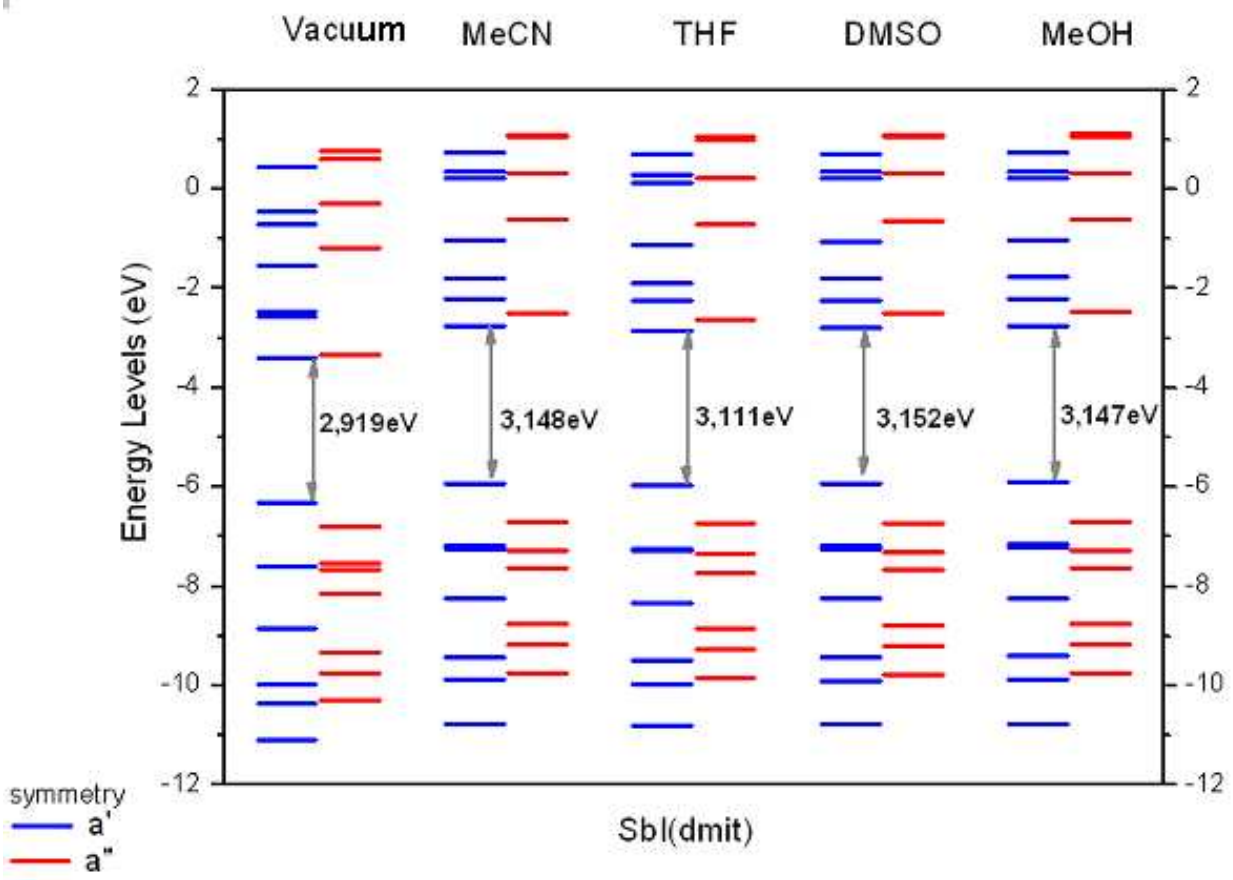

Figure 2S. Energy levels diagrams of [SbI(dmit)], with SCF molecular orbitals within the B3LYP and B3LYP-CPCM methods.

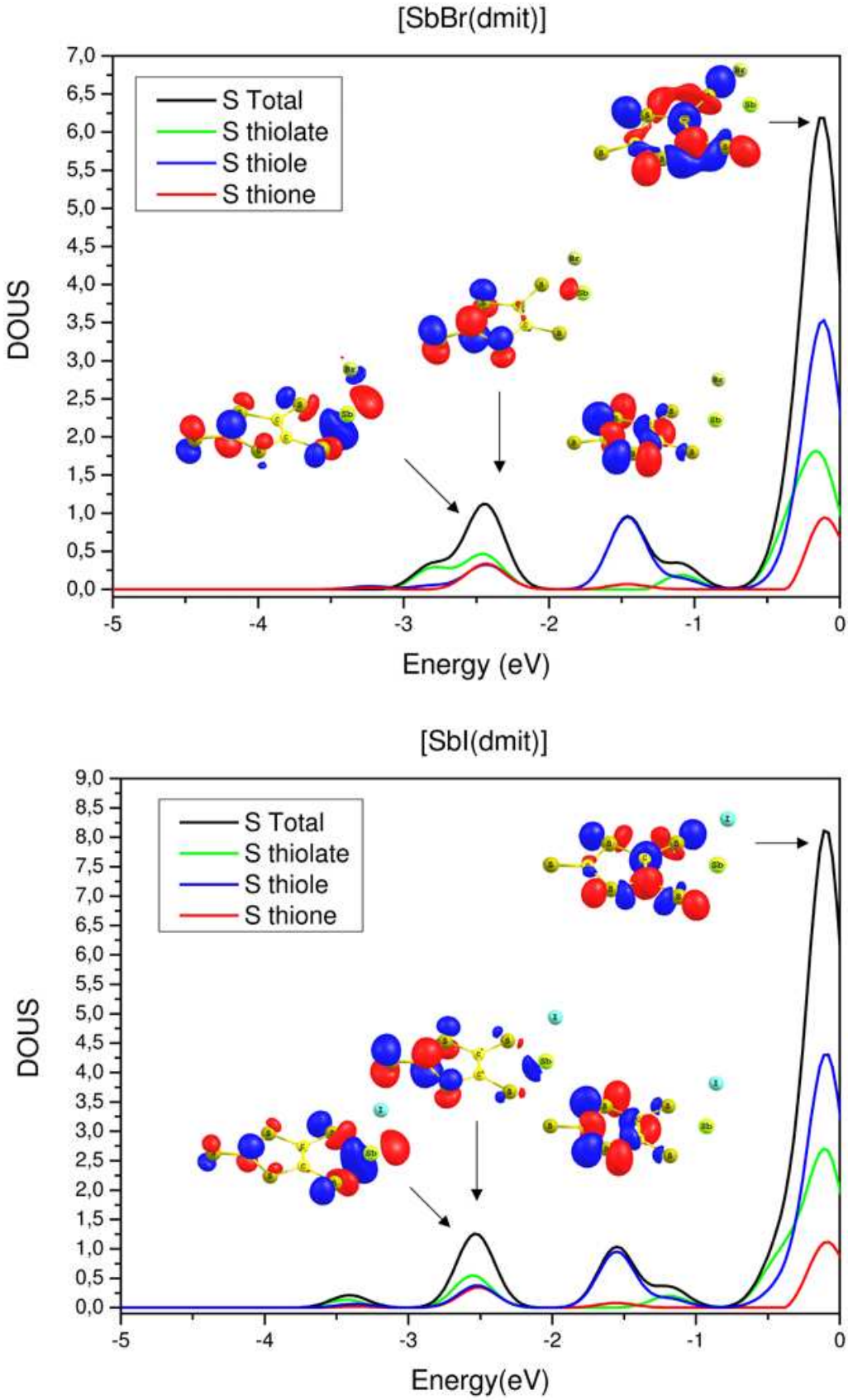

Figure 3S. Unoccupied Density of States Diagram (DOUS) of the complexes [SbL(dmit)] (L= Br or I), with the B3LYP method.