Electronic Supplementary Information

Experimental and computational studies of the optical properties of 2,5,8-tris(phenylthiolato)heptazine with an inverted singlet-triplet gap

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Table S1: Selected bond lengths (in Å) and angles (in °) of molecules **1-4**.

		X-ray structure	Computational model
Molecule **1**	S-C(Hz)	1.742(3)	1.74
	S-C(Ph)	1.755(3)	1.77
	C(Hz)-S-C(Ph)	103.43(17)	102.4
	S-C(Hz)-N(Hz)	119.(2), 111.3(2)	119.5, 112.4
Molecule **2**	O-C(Hz)	1.345(7), 1.335(8), 1.321(7)	1.33
	O-C(Ph)	1.414(8), 1.412(8), 1.406(8)	1.39
	C(Hz)-O-C(Ph)	120.0(7), 119.4(7), 118.8(7)	119.2
	O-C(Hz)-N(Hz)	119.7(9)-110.4(10)	118.3, 113.2
Molecule **3**	Se-C(Hz)	1.891(5)	1.89
	Se-C(Ph)	1.895(4)	1.91
	C(Hz)-Se-C(Ph)	99.1(2)	99.4
	Se-C(Hz)-N(Hz)	118.8(4), 111.3(2)	119.1, 112.6
Molecule **4**	Te-C(Hz)	-	2.09
	Te-C(Ph)	-	2.10
	C(Hz)-Te-C(Ph)	-	97.5
	Te-C(Hz)-N(Hz)	-	119.3, 112.7

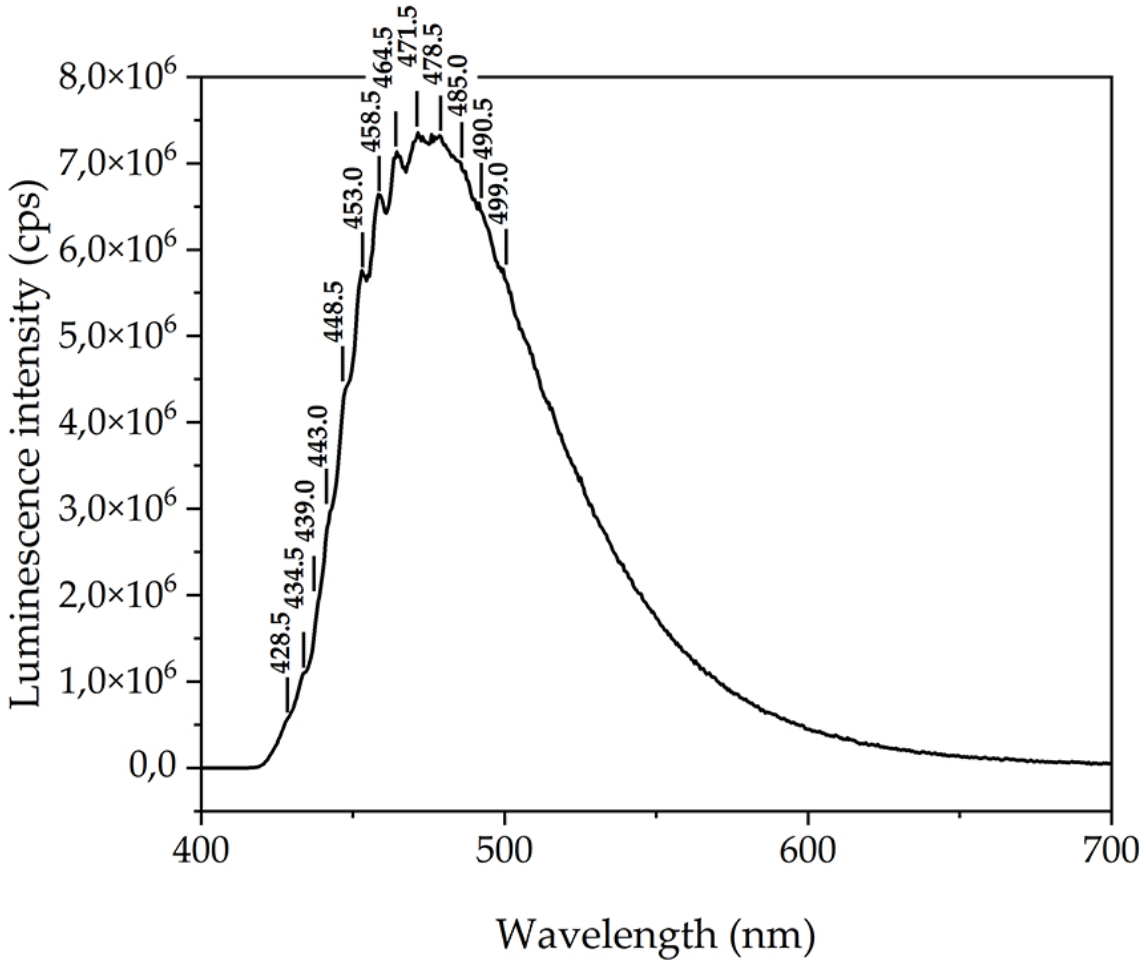


Figure S1: Emission spectrum of molecule **1** in the solid state at 78 K (λ_{ex} of 375 nm) revealing the vibronic profile of the ground state (in nm).

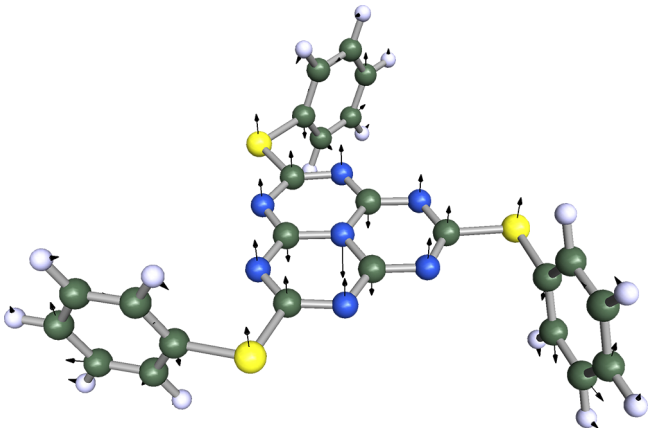


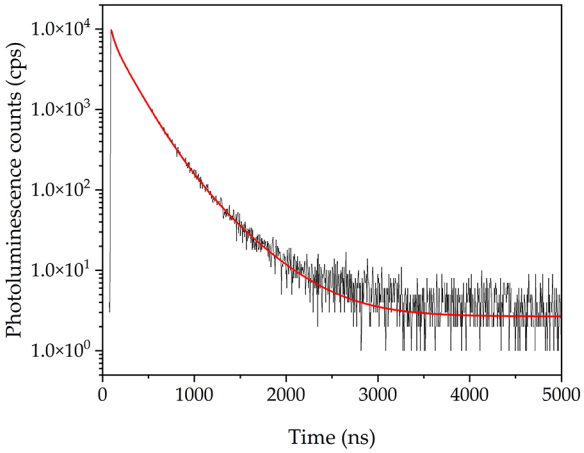
Figure S2: Atomic displacements (black arrows) of the symmetric out-of-plane vibrational mode ($\tilde{\nu}$ of 266.11 cm^{-1}) of molecule **1**.

Table S2: The fitting parameters A, B_i and τ_i (in s) of the transient photoluminiscence decay data of molecule **1** in the solid state at different temperatures (in K).

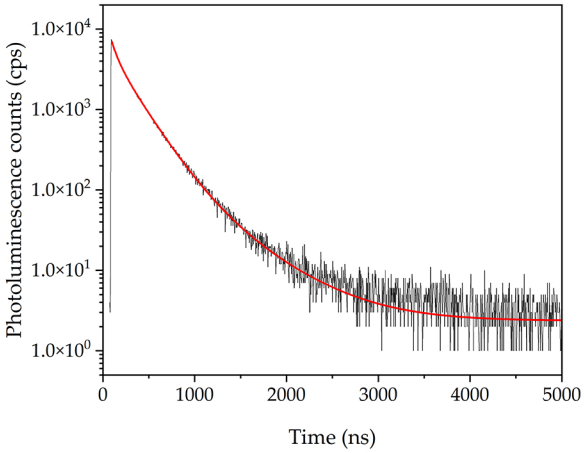
Temperature	A	B_1	τ_1	B_2	τ_2	B_3	τ_3	χ^2	$\langle\tau\rangle_{amp}$
300	2.668E+0	2.726E+3	3.703E−8	6.537E+3	1.971E−7	7.429E+2	4.301E−7	1.236	1.708E−7
280	2.357E+0	2.417E+3	5.898E−8	4.500E+3	2.279E−7	3.070E+2	5.453E−7	1.123	1.848E−7
260	4.936E+0	3.944E+3	6.666E−8	5.654E+3	2.481E−7	4.378E+2	5.997E−7	1.189	1.921E−7
240	3.939E+0	4.738E+3	9.879E−8	4.835E+3	2.955E−7	2.136E+2	9.371E−7	1.171	2.143E−7
220	3.851E+0	4.607E+3	2.049E−7	4.020E+2	7.584E−7	-	-	1.455	2.493E−7
200	5.403E+0	5.101E+3	2.406E−7	1.892E+2	1.087E−6	-	-	1.459	2.708E−7
180	5.726E+0	5.248E+3	2.809E−7	1.019E+2	1.263E−6	-	-	1.308	2.996E−7
160	1.213E+1	6.419E+3	2.719E−7	1.834E+3	4.895E−7	-	-	1.148	3.203E−7
140	8.413E+0	2.832E+3	2.664E−7	2.575E+3	4.486E−7	-	-	1.112	3.532E−7
120	1.014E+1	2.849E+3	2.625E−7	5.740E+3	4.461E−7	-	-	1.174	3.852E−7
100	6.378E+0	1.504E+3	2.549E−7	4.800E+3	4.656E−7	-	-	1.036	4.153E−7
78	5.011E+0	7.291E+3	3.973E−7	2.468E+3	5.849E−7	-	-	1.115	4.447E−7

Table S3: The fitting parameters A, B and τ (in s) of the transient photoluminiscence decay data of molecule **1** in toluene solution in the absence and presence of oxygen.

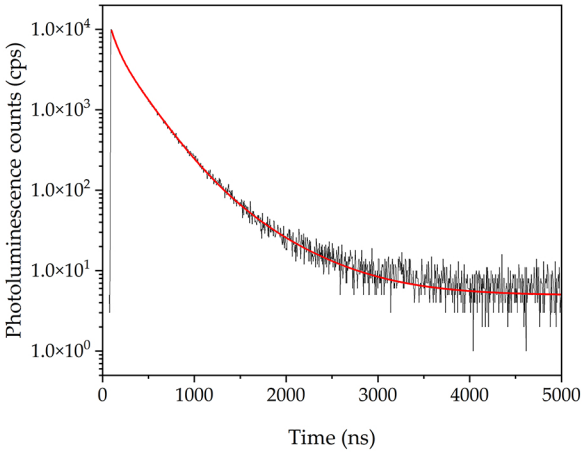
Temperature	A	B	χ^2	τ
O_2 free	3.199E+1	4.997E+2	1.087	4.620E−7
O_2 saturated	1.985E+1	2.544E+2	1.104	3.163E−7



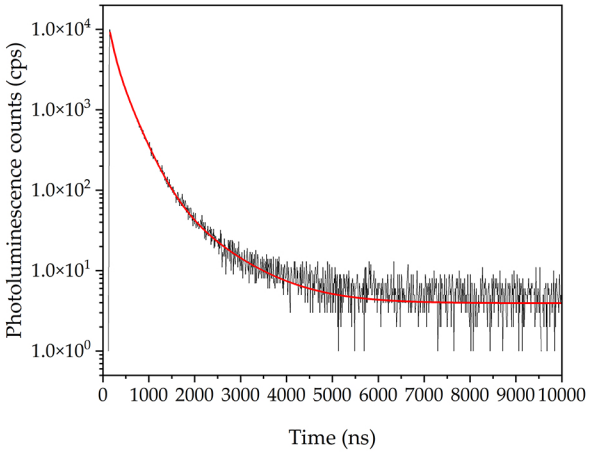
T = 300 K, $\langle\tau\rangle_{amp}$ = 171 ns, χ^2 = 1.24



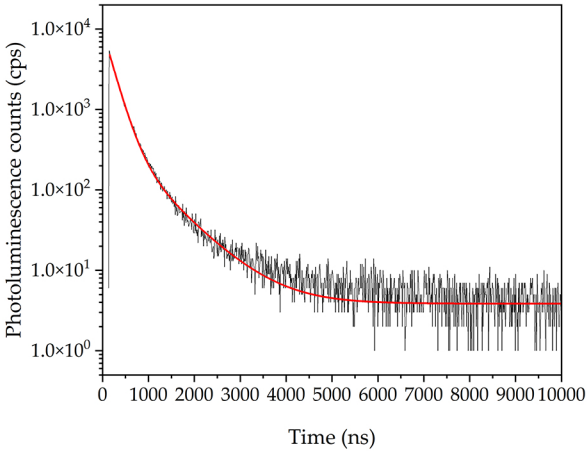
T = 280 K, $\langle\tau\rangle_{amp}$ = 185 ns, χ^2 = 1.12



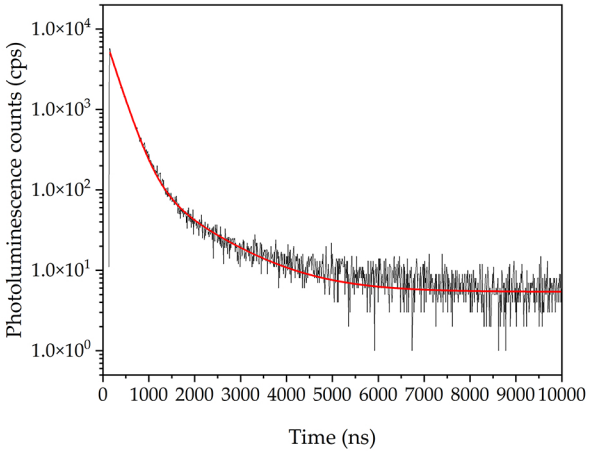
T = 260 K, $\langle\tau\rangle_{amp}$ = 192 ns, χ^2 = 1.19



T = 240 K, $\langle\tau\rangle_{amp}$ = 214 ns, χ^2 = 1.17

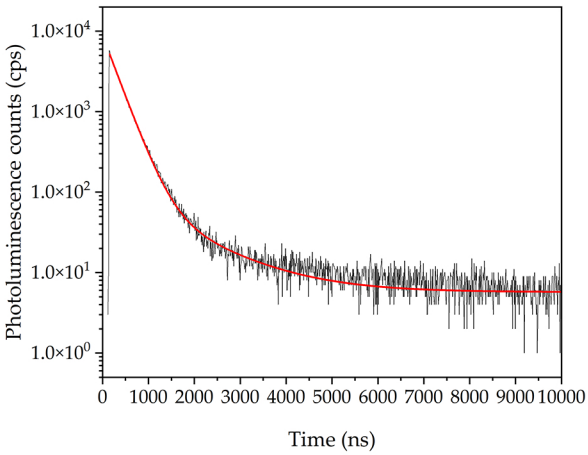


T = 220 K, $\langle\tau\rangle_{amp}$ = 249 ns, χ^2 = 1.46

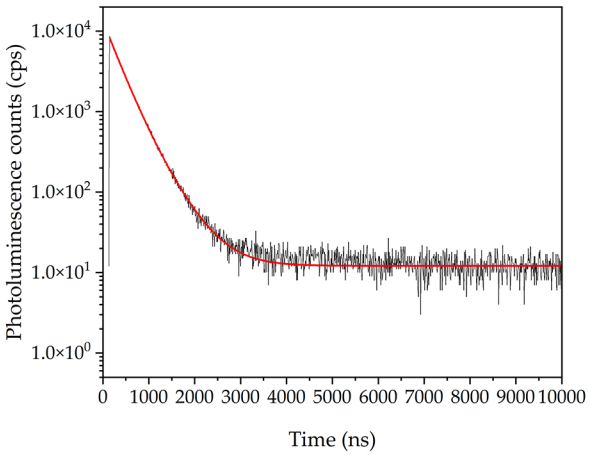


T = 200 K, $\langle\tau\rangle_{amp}$ = 271 ns, χ^2 = 1.46

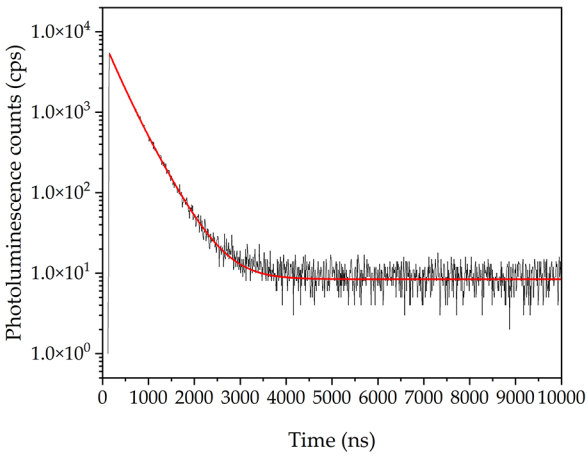
Figure S3: Transient photoluminescence decay data of molecule **1** in the solid state.



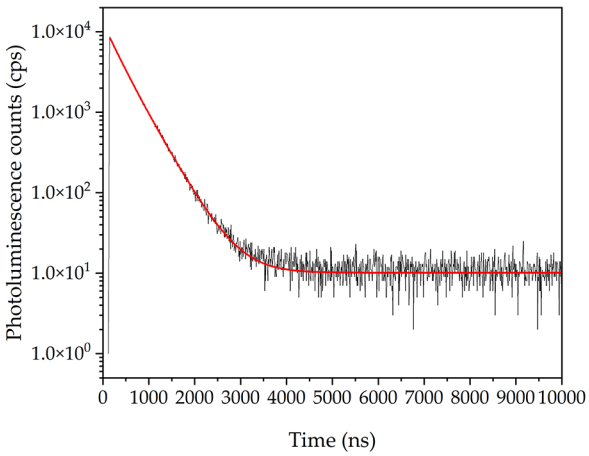
T = 180 K, $\langle\tau\rangle_{amp}$ = 300 ns, χ^2 = 1.31



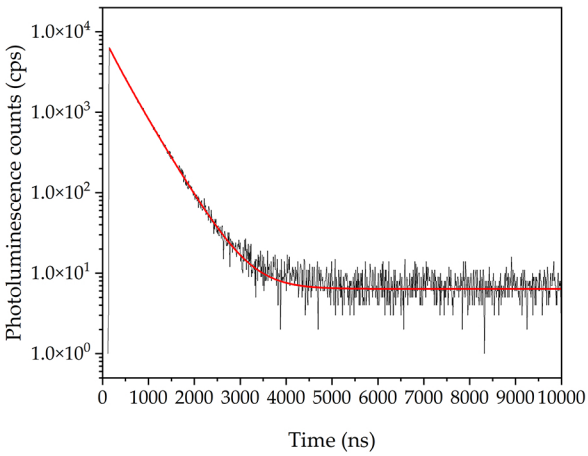
T = 160 K, $\langle\tau\rangle_{amp}$ = 320 ns, χ^2 = 1.15



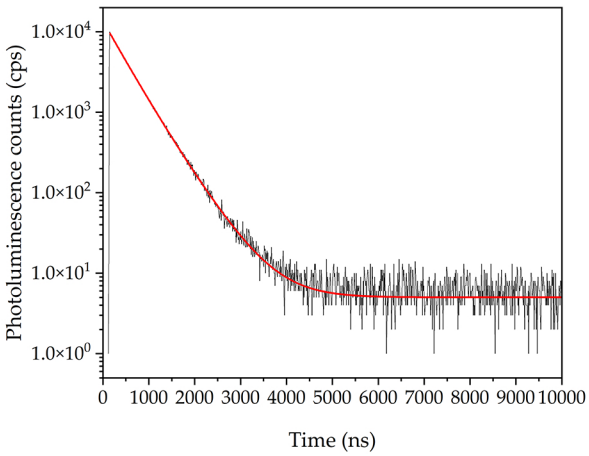
T = 140 K, $\langle\tau\rangle_{amp}$ = 353 ns, χ^2 = 1.11



T = 120 K, $\langle\tau\rangle_{amp}$ = 385 ns, χ^2 = 1.17



T = 100 K, $\langle\tau\rangle_{amp}$ = 415 ns, χ^2 = 1.04



T = 78 K, $\langle\tau\rangle_{amp}$ = 445 ns, χ^2 = 1.12

Figure S4: Transient photoluminescence decay data of molecule **1** in the solid state (continuation).

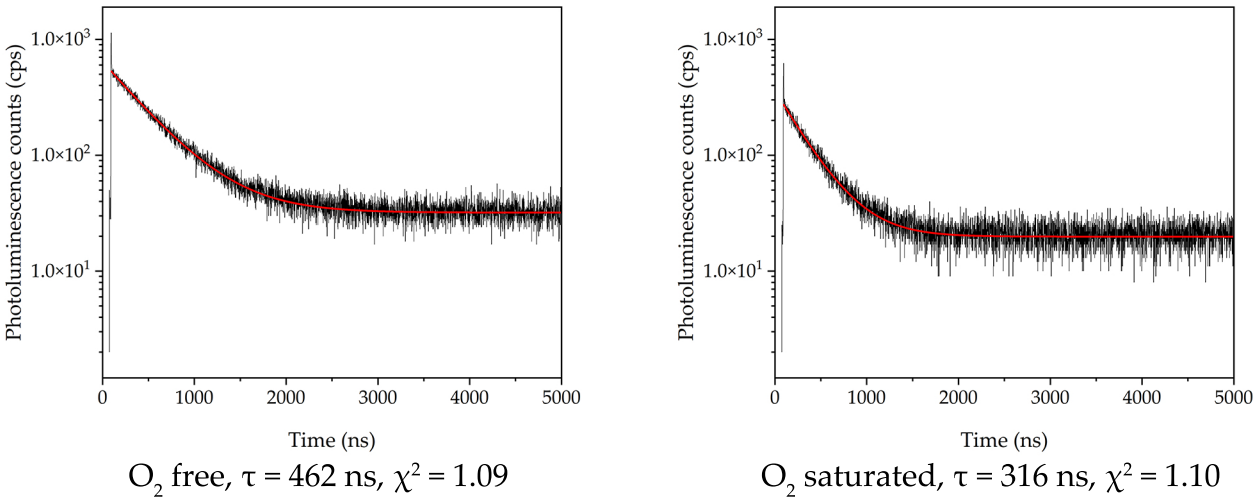


Figure S5: Transient photoluminescence decay data of molecule **1** in toluene solution.

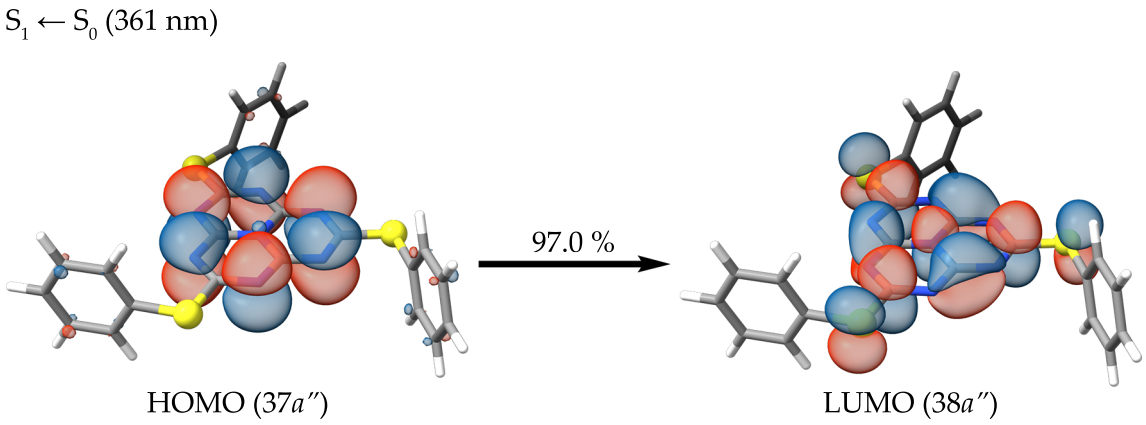


Figure S6: Molecular orbitals of the S_1 transition at the TD-DFT/PBE0/def2-TZVP level of theory of molecule **1**.

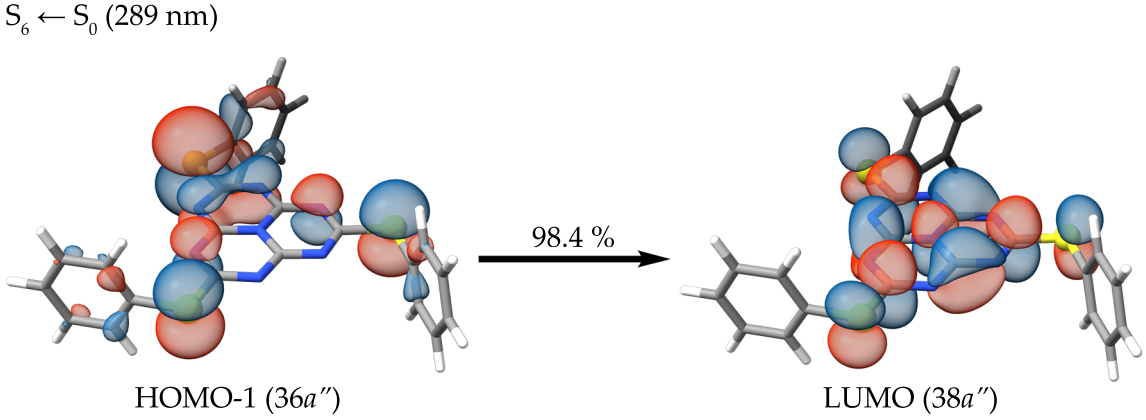


Figure S7: Molecular orbitals of the S_6 transition at the TD-DFT/PBE0/def2-TZVP level of theory of molecule **1**.

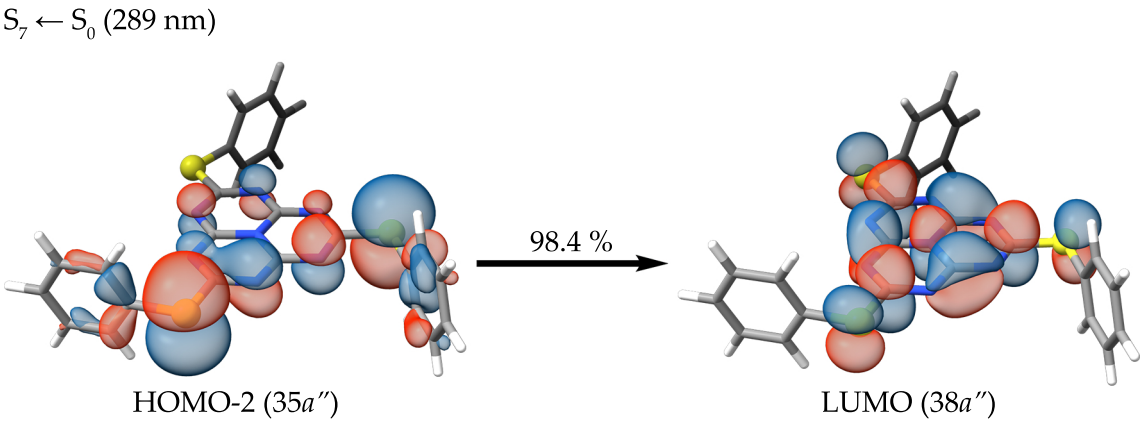


Figure S8: Molecular orbitals of the S_7 transition at the TD-DFT/PBE0/def2-TZVP level of theory of molecule **1**.

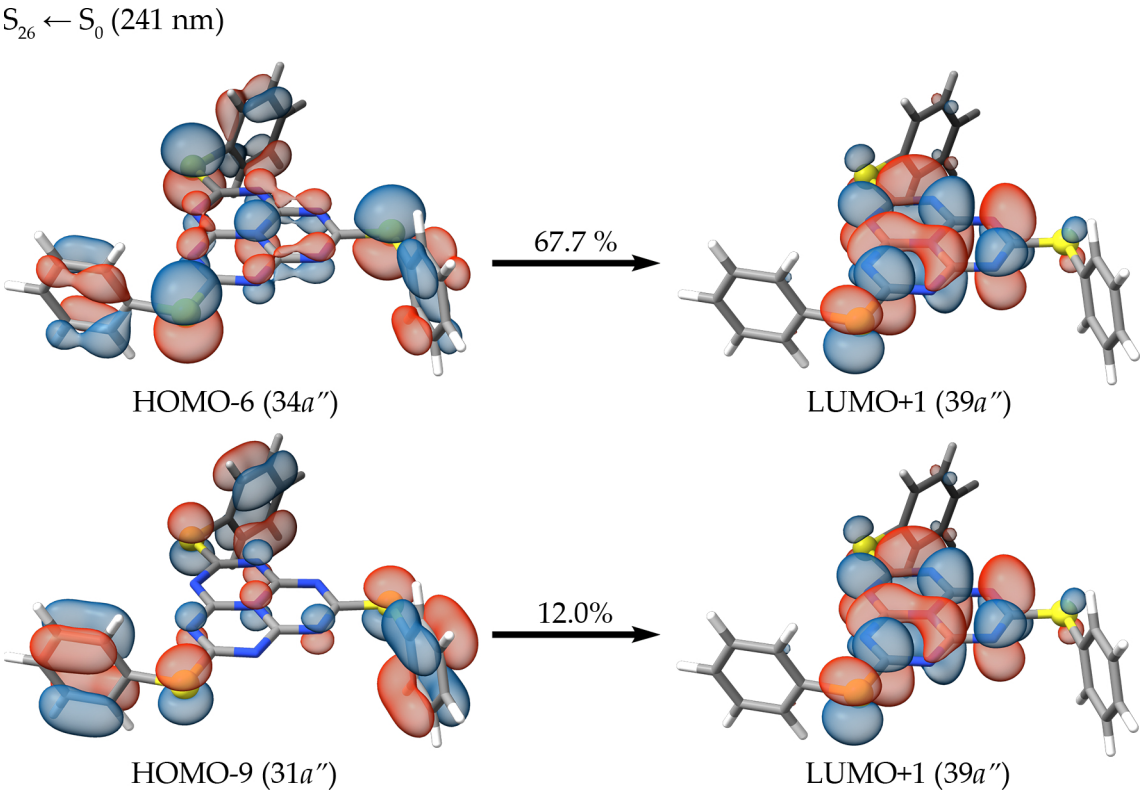


Figure S9: Molecular orbitals of the S_{26} transition at the TD-DFT/PBE0/def2-TZVP level of theory of molecule **1**.

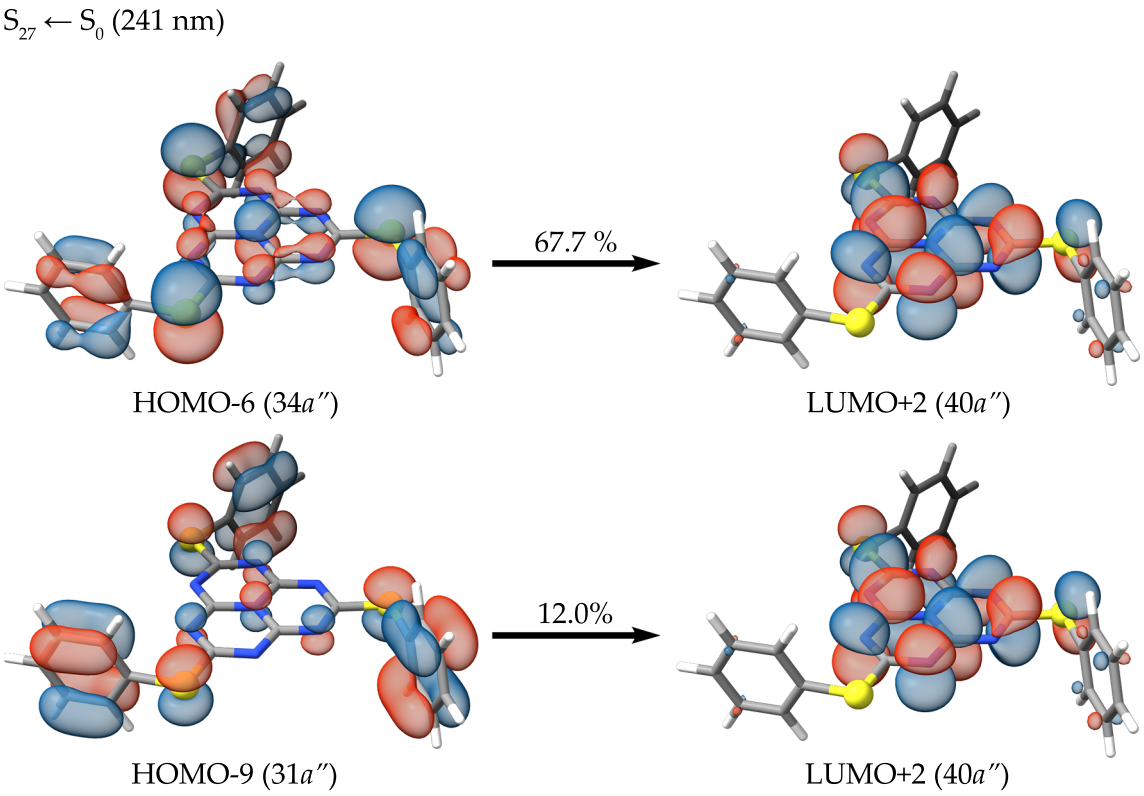


Figure S10: Molecular orbitals of the S_{27} transition at the TD-DFT/PBE0/def2-TZVP level of theory of molecule **1**.

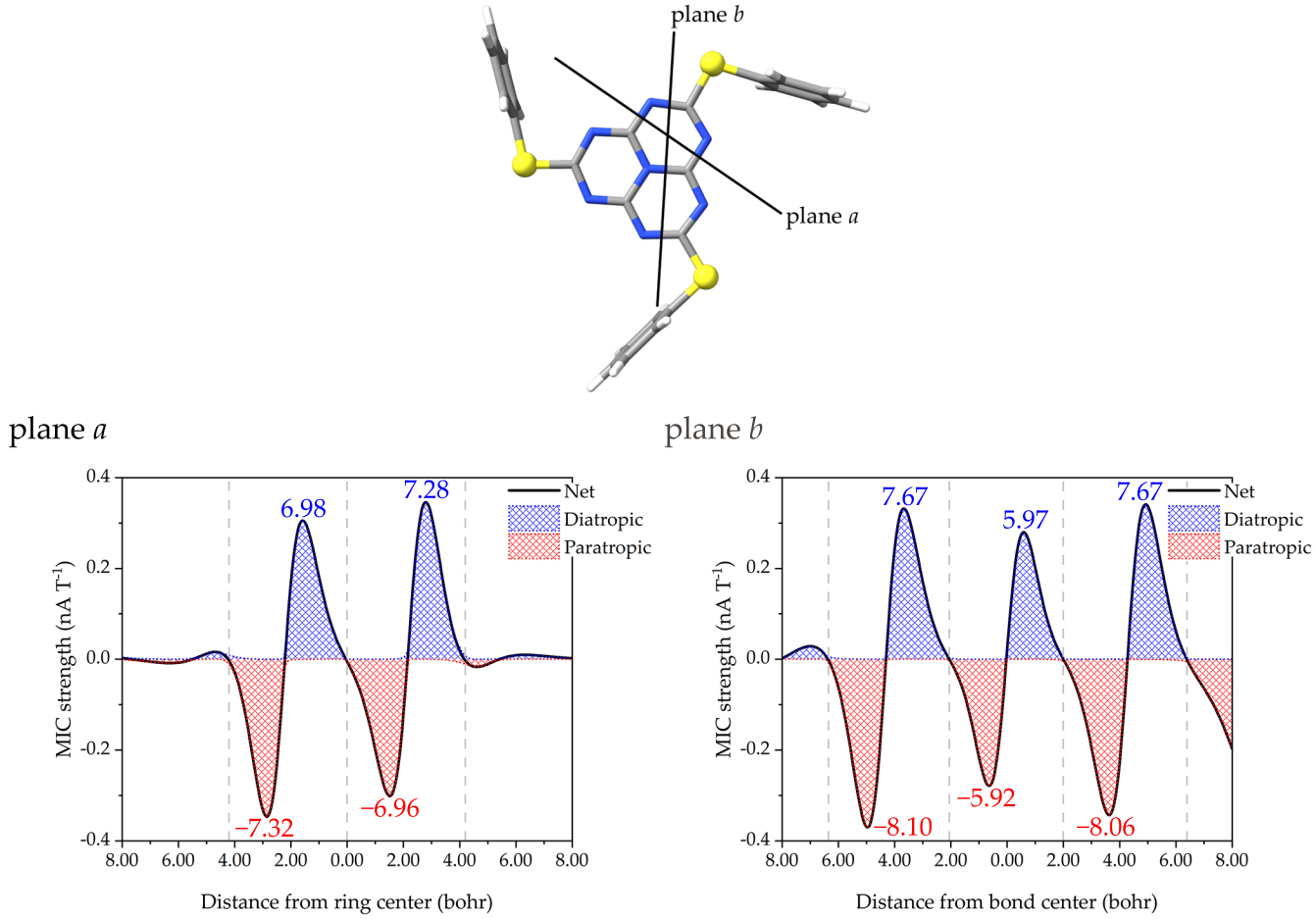


Figure S11: (Top) Selected cut planes. (Bottom) The net (black), diatropic (blue), and paratropic (red) MIC density profile along the selected cut planes. The vertical dashed grey lines indicate numerical integration limits.

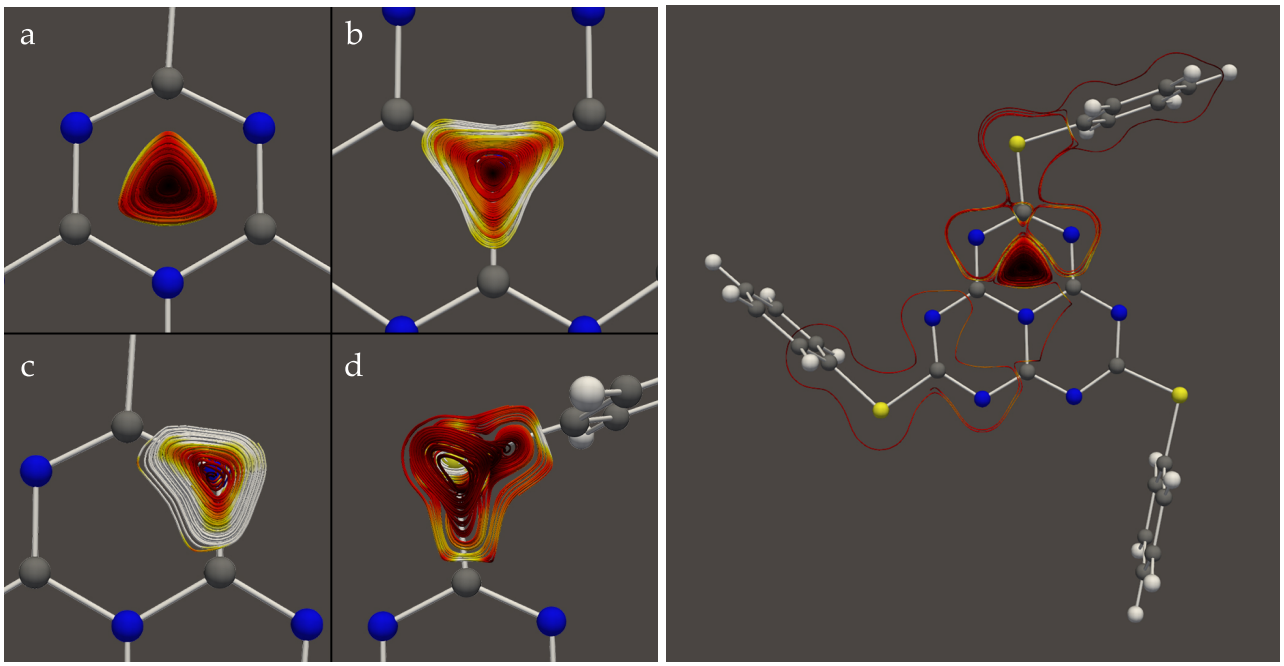


Figure S12: (Left) Streamline representations of the MIC density at (a) the center of a triazine ring, (b) the central nitrogen atom, (c) a peripheral nitrogen atom, and (d) a sulfur atom of molecule **1**. (Right) Electron delocalization pathways of molecule **1**. The MIC strength increases in the order black-red-orange-yellow-white.

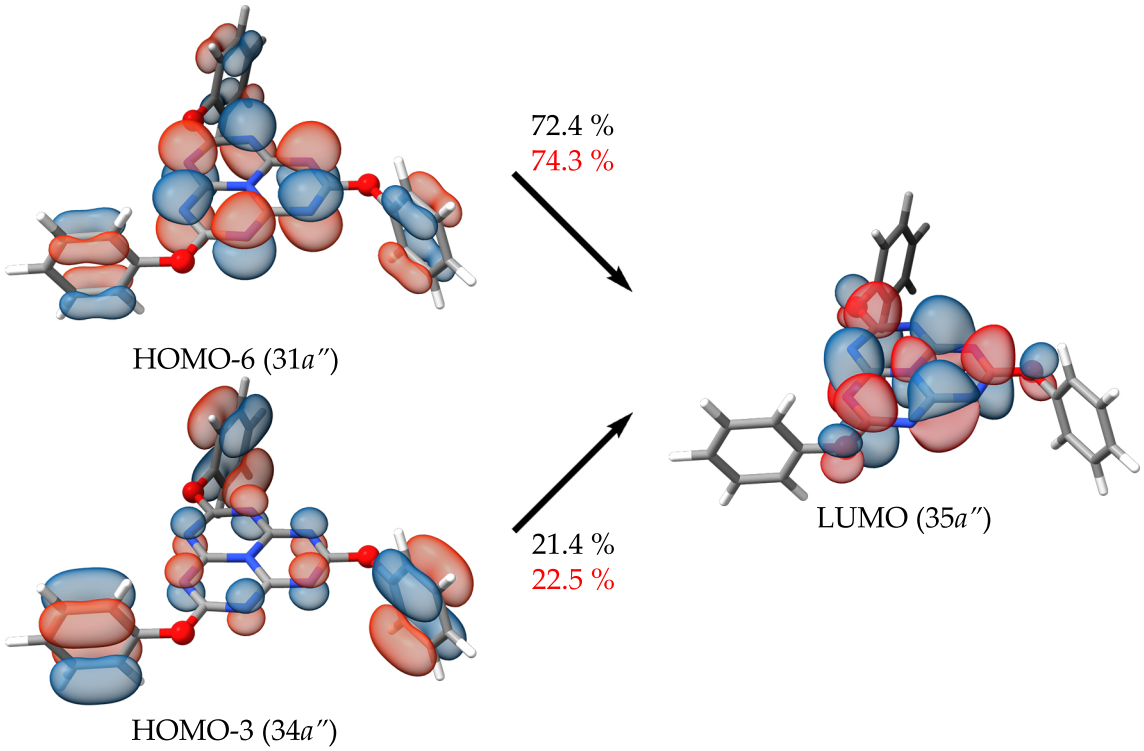


Figure S13: Molecular orbitals and their contribution to the S_1 (T_1 in red) transition at the ADC(2)/def2-TZVP level of theory of molecule **2**.

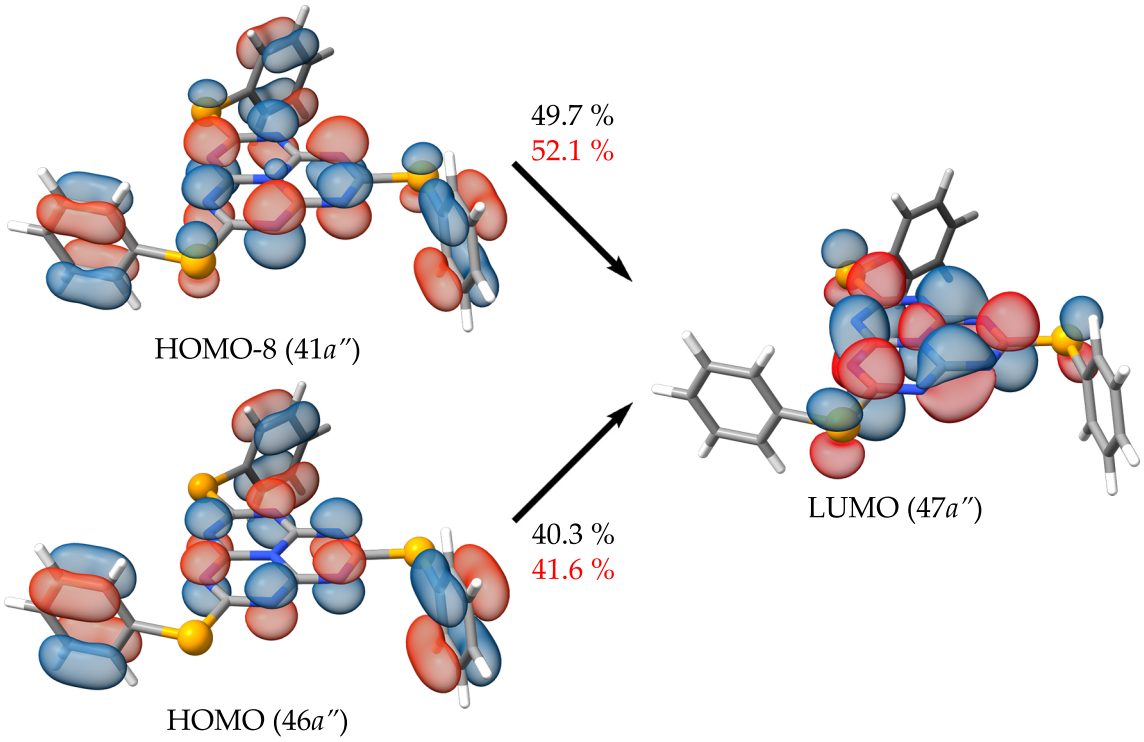


Figure S14: Molecular orbitals and their contribution to the S_1 (T_1 in red) transition at the ADC(2)/def2-TZVP level of theory of molecule **3**.

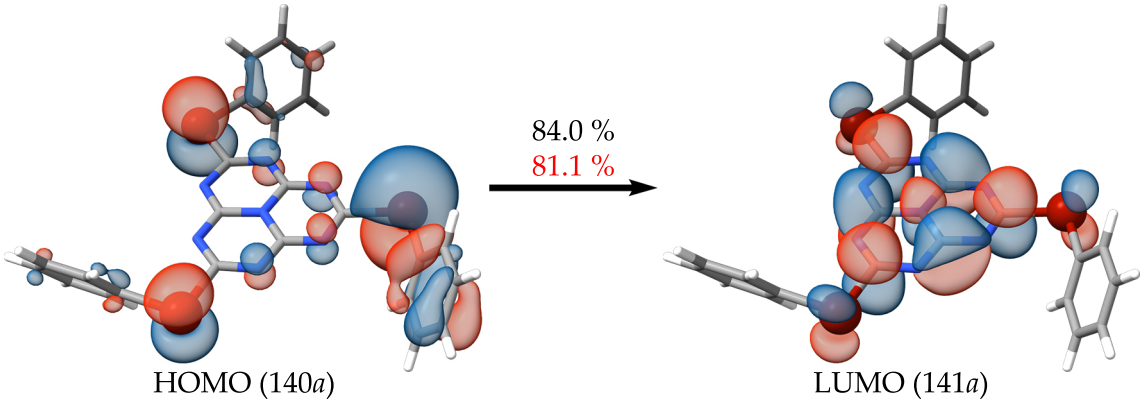


Figure S15: Molecular orbitals and their contribution to the S_1 (T_1 in red) transition at the ADC(2)/def2-TZVP level of theory of molecule **4**.

Cartesian coordinates of molecule 1 (S_0 geometry).

C	1.0779213	0.8881808	0.0000000
C	-0.4263747	2.5654747	0.0000000
C	-1.3081478	0.4894168	0.0000000
C	-2.0085789	-1.6519887	0.0000000
C	0.2302265	-1.3775976	0.0000000
C	2.4349536	-0.9134860	0.0000000
N	-1.5115247	1.7915535	0.0000000
N	0.8420768	2.1914415	0.0000000
N	-2.3188825	-0.3664608	0.0000000
N	-0.7957685	-2.2047956	0.0000000
N	1.4768056	-1.8249807	0.0000000
N	2.3072932	0.4132420	0.0000000
N	0.0000000	0.0000000	0.0000000
S	-0.8216102	4.2621921	0.0000000
S	4.1019717	-1.4195608	0.0000000
S	-3.2803615	-2.8426313	0.0000000
C	0.7732184	5.0237814	0.0000000
C	1.3848354	5.3439403	-1.2052049
C	1.3848354	5.3439403	1.2052049
C	2.6195910	5.9723011	-1.2020348
H	0.8951387	5.0921781	-2.1379346
C	2.6195910	5.9723011	1.2020348
H	0.8951387	5.0921781	2.1379346
C	3.2372399	6.2851398	0.0000000
H	3.1012326	6.2160553	-2.1415548
H	3.1012326	6.2160553	2.1415548
H	4.2036529	6.7755310	0.0000000
C	3.9641131	-3.1815175	0.0000000
C	3.9355703	-3.8712728	1.2052049
C	3.9355703	-3.8712728	-1.2052049
C	3.8623689	-5.2547829	1.2020348
H	3.9623862	-3.3213019	2.1379346
C	3.8623689	-5.2547829	-1.2020348
H	3.9623862	-3.3213019	-2.1379346
C	3.8244708	-5.9461019	0.0000000
H	3.8326455	-5.7937739	2.1415548
H	3.8326455	-5.7937739	-2.1415548
H	3.7659556	-7.0282357	0.0000000
C	-4.7373315	-1.8422639	0.0000000
C	-5.3204057	-1.4726675	1.2052049
C	-5.3204057	-1.4726675	-1.2052049
C	-6.4819599	-0.7175182	1.2020348
H	-4.8575249	-1.7708762	2.1379346
C	-6.4819599	-0.7175182	-1.2020348
H	-4.8575249	-1.7708762	-2.1379346
C	-7.0617107	-0.3390379	0.0000000
H	-6.9338782	-0.4222814	2.1415548
H	-6.9338782	-0.4222814	-2.1415548
H	-7.9696085	0.2527047	0.0000000

Cartesian coordinates of molecule 1 (S_1 geometry).

C	1.1906537	0.7166684	0.2937449
C	-0.0434568	2.6187389	0.3060107
C	-1.2159799	0.6728021	0.2937449
C	-2.2461660	-1.3470042	0.3060107
C	0.0253262	-1.3894706	0.2937449
C	2.2896228	-1.2717347	0.3060107
N	-1.2176891	1.9835783	0.4160277
N	1.1501957	2.0268575	0.4053269
N	-2.3304079	-0.0173301	0.4053269
N	-1.1089847	-2.0463389	0.4160277
N	1.1802122	-2.0095274	0.4053269
N	2.3266738	0.0627605	0.4160277
N	-0.0000000	0.0000000	-0.0008556
S	-0.1855240	4.3524692	0.1994066
S	3.8621109	-2.0155661	0.1994066
S	-3.6765869	-2.3369031	0.1994066
C	1.4946210	4.8689654	0.0231541
C	1.8967878	5.4220444	-1.1863412
C	2.3840153	4.7919390	1.0892844
C	3.1921147	5.8966158	-1.3295781
H	1.1955069	5.4734105	-2.0104872
C	3.6789975	5.2546052	0.9350366
H	2.0606431	4.3606001	2.0278408
C	4.0835530	5.8095834	-0.2718271
H	3.5049449	6.3279316	-2.2731104
H	4.3754325	5.1845168	1.7621267
H	5.0973993	6.1748616	-0.3863214
C	3.4693372	-3.7288624	0.0231541
C	2.9579333	-4.4605873	1.0892844
C	3.7472343	-4.3536886	-1.1863412
C	2.7111228	-5.8134079	0.9350366
H	2.7460689	-3.9648693	2.0278408
C	3.5105617	-5.7127603	-1.3295781
H	4.1423591	-3.7720446	-2.0104872
C	2.9894703	-6.4412523	-0.2718271
H	2.3022070	-6.3814941	1.7621267
H	3.7276771	-6.1993371	-2.2731104
H	2.7988873	-7.5019081	-0.3863214
C	-4.9639582	-1.1401029	0.0231541
C	-5.3419486	-0.3313517	1.0892844
C	-5.6440221	-1.0683558	-1.1863412
C	-6.3901203	0.5588027	0.9350366
H	-4.8067120	-0.3957307	2.0278408
C	-6.7026764	-0.1838555	-1.3295781
H	-5.3378659	-1.7013659	-2.0104872
C	-7.0730233	0.6316690	-0.2718271
H	-6.6776395	1.1969773	1.7621267
H	-7.2326220	-0.1285945	-2.2731104
H	-7.8962867	1.3270465	-0.3863214

Cartesian coordinates of molecule 1 (T_1 geometry).

C	1.1998550	0.7095530	0.2702971
C	-0.0185614	2.6192809	0.2853263
C	-1.2144185	0.6843284	0.2702971
C	-2.2590831	-1.3257151	0.2853263
C	0.0145634	-1.3938815	0.2702971
C	2.2776445	-1.2935658	0.2853263
N	-1.2035630	1.9969520	0.3743963
N	1.1734474	2.0210405	0.3623513
N	-2.3369962	0.0057150	0.3623513
N	-1.1276297	-2.0407921	0.3743963
N	1.1635487	-2.0267555	0.3623513
N	2.3311926	0.0438401	0.3743963
N	-0.0000000	0.0000000	0.0238256
S	-0.1591876	4.3565606	0.2070907
S	3.8524860	-2.0404198	0.2070907
S	-3.6932984	-2.3161408	0.2070907
C	1.5162991	4.8846326	0.0313082
C	1.8861130	5.5261351	-1.1447435
C	2.4333463	4.7357951	1.0663442
C	3.1753320	6.0176702	-1.2855948
H	1.1643893	5.6322216	-1.9457378
C	3.7222169	5.2150793	0.9128622
H	2.1366973	4.2367888	1.9796354
C	4.0940773	5.8587632	-0.2601285
H	3.4621068	6.5179245	-2.2030157
H	4.4396629	5.0888198	1.7149596
H	5.1033887	6.2367700	-0.3732839
C	3.4720664	-3.7554698	0.0313082
C	2.8846457	-4.4752373	1.0663442
C	3.8427169	-4.3964893	-1.1447435
C	2.6552827	-5.8310740	0.9128622
H	2.6008181	-3.9688286	1.9796354
C	3.6237893	-5.7587533	-1.2855948
H	4.2954524	-3.8245015	-1.9457378
C	3.0267991	-6.4749566	-0.2601285
H	2.1872157	-6.3892707	1.7149596
H	3.9136348	-6.2572347	-2.2030157
H	2.8495069	-7.5380493	-0.3732839
C	-4.9883654	-1.1291628	0.0313082
C	-5.3179920	-0.2605579	1.0663442
C	-5.7288299	-1.1296458	-1.1447435
C	-6.3774996	0.6159948	0.9128622
H	-4.7375154	-0.2679603	1.9796354
C	-6.7991213	-0.2589169	-1.2855948
H	-5.4598417	-1.8077201	-1.9457378
C	-7.1208765	0.6161934	-0.2601285
H	-6.6268786	1.3004510	1.7149596
H	-7.3757416	-0.2606898	-2.2030157
H	-7.9528956	1.3012793	-0.3732839

Cartesian coordinates of molecule 2.

C	1.1757263	0.7521365	0.0000000
C	-0.1246016	2.5891192	0.0000000
C	-1.2392325	0.6421406	0.0000000
C	-2.1799422	-1.4024678	0.0000000
C	0.0635062	-1.3942771	0.0000000
C	2.3045438	-1.1866514	0.0000000
N	-1.2922162	1.9573636	0.0000000
N	1.0915089	2.0729680	0.0000000
N	-2.3409974	-0.0912096	0.0000000
N	-1.0490185	-2.0977739	0.0000000
N	1.2494885	-1.9817584	0.0000000
N	2.3412347	0.1404103	0.0000000
N	0.0000000	0.0000000	0.0000000
O	-0.2459021	3.9085869	0.0000000
O	3.5078867	-1.7413360	0.0000000
O	-3.2619845	-2.1672510	0.0000000
C	0.9018368	4.6971532	0.0000000
C	1.4279931	5.1129125	-1.2069039
C	1.4279931	5.1129125	1.2069039
C	2.5232537	5.9625806	-1.2009779
H	0.9825288	4.7708337	-2.1327452
C	2.5232537	5.9625806	1.2009779
H	0.9825288	4.7708337	2.1327452
C	3.0725924	6.3867847	0.0000000
H	2.9481166	6.2936719	-2.1410353
H	2.9481166	6.2936719	2.1410353
H	3.9285545	7.0507439	0.0000000
C	3.6169357	-3.1295902	0.0000000
C	3.7139155	-3.7931346	1.2069039
C	3.7139155	-3.7931346	-1.2069039
C	3.9021194	-5.1664921	1.2009779
H	3.6403987	-3.2363118	2.1327452
C	3.9021194	-5.1664921	-1.2009779
H	3.6403987	-3.2363118	-2.1327452
C	3.9948216	-5.8543354	0.0000000
H	3.9764214	-5.6999798	2.1410353
H	3.9764214	-5.6999798	-2.1410353
H	4.1418461	-6.9275999	0.0000000
C	-4.5187724	-1.5675631	0.0000000
C	-5.1419087	-1.3197779	1.2069039
C	-5.1419087	-1.3197779	-1.2069039
C	-6.4253731	-0.7960885	1.2009779
H	-4.6229276	-1.5345219	2.1327452
C	-6.4253731	-0.7960885	-1.2009779
H	-4.6229276	-1.5345219	-2.1327452
C	-7.0674140	-0.5324493	0.0000000
H	-6.9245381	-0.5936921	2.1410353
H	-6.9245381	-0.5936921	-2.1410353
H	-8.0704005	-0.1231440	0.0000000

Cartesian coordinates of molecule 3.

C	1.0517112	0.9192832	0.0000000
C	-0.5001002	2.5504421	0.0000000
C	-1.3219782	0.4511670	0.0000000
C	-1.9586975	-1.7083205	0.0000000
C	0.2702670	-1.3704502	0.0000000
C	2.4587977	-0.8421215	0.0000000
N	-1.5616570	1.7486379	0.0000000
N	0.7773053	2.2151959	0.0000000
N	-2.3070686	-0.4344318	0.0000000
N	-0.7335364	-2.2267536	0.0000000
N	1.5297633	-1.7807641	0.0000000
N	2.2951933	0.4781157	0.0000000
N	-0.0000000	0.0000000	0.0000000
Se	-0.9714075	4.3801555	0.0000000
Se	4.2790297	-1.3488142	0.0000000
Se	-3.3076222	-3.0313413	0.0000000
C	0.7751618	5.1533190	0.0000000
C	1.3987296	5.4454870	-1.2052236
C	1.3987296	5.4454870	1.2052236
C	2.6594126	6.0220598	-1.2017976
H	0.9029534	5.2138670	-2.1399487
C	2.6594126	6.0220598	1.2017976
H	0.9029534	5.2138670	2.1399487
C	3.2895145	6.3092193	0.0000000
H	3.1511143	6.2444587	-2.1415301
H	3.1511143	6.2444587	2.1415301
H	4.2758693	6.7582151	0.0000000
C	4.0753243	-3.2479693	0.0000000
C	4.0165652	-3.9340789	1.2052236
C	4.0165652	-3.9340789	-1.2052236
C	3.8855505	-5.3141488	1.2017976
H	4.0638646	-3.3889141	2.1399487
C	3.8855505	-5.3141488	-1.2017976
H	4.0638646	-3.3889141	-2.1399487
C	3.8191869	-6.0034128	0.0000000
H	3.8323027	-5.8511744	2.1415301
H	3.8323027	-5.8511744	-2.1415301
H	3.7148513	-7.0821190	0.0000000
C	-4.8504861	-1.9053497	0.0000000
C	-5.4152948	-1.5114081	1.2052236
C	-5.4152948	-1.5114081	-1.2052236
C	-6.5449631	-0.7079110	1.2017976
H	-4.9668180	-1.8249529	2.1399487
C	-6.5449631	-0.7079110	-1.2017976
H	-4.9668180	-1.8249529	-2.1399487
C	-7.1087014	-0.3058065	0.0000000
H	-6.9834170	-0.3932843	2.1415301
H	-6.9834170	-0.3932843	-2.1415301
H	-7.9907206	0.3239038	0.0000000

Cartesian coordinates of molecule 4.

C	1.1795962	-0.7483019	-0.1368837
C	2.3081074	1.2033786	-0.1376090
C	0.0582503	1.3957112	-0.1368837
C	-2.1962102	1.3971904	-0.1376090
C	-1.2378466	-0.6474094	-0.1368837
C	-0.1118973	-2.6005690	-0.1376090
N	1.2363230	1.9928093	-0.1406307
N	2.3447425	-0.1170887	-0.1389554
N	-1.0709694	2.0891510	-0.1389554
N	-2.3439850	0.0742824	-0.1406307
N	-1.2737731	-1.9720622	-0.1389554
N	1.1076620	-2.0670917	-0.1406307
N	-0.0000000	-0.0000000	-0.1325551
Te	4.1021996	2.2780199	-0.1546961
Te	-0.0782767	-4.6916190	-0.1546961
Te	-4.0239229	2.4135991	-0.1546961
C	5.4074673	0.6332594	-0.0531819
C	5.4765155	-0.2822188	-1.0969725
C	6.2222740	0.4823760	1.0626159
C	6.3511762	-1.3537404	-1.0146209
H	4.8409490	-0.1668412	-1.9659706
C	7.1080626	-0.5837127	1.1314828
H	6.1596411	1.1875698	1.8832160
C	7.1700187	-1.5029363	0.0958142
H	6.3945823	-2.0735272	-1.8237043
H	7.7421969	-0.6996792	2.0027827
H	7.8563454	-2.3396891	0.1541669
C	-2.1553149	-4.9996338	-0.0531819
C	-2.6933871	-5.6298354	1.0626159
C	-2.9826664	-4.6016921	-1.0969725
C	-4.0595413	-5.8639064	1.1314828
H	-2.0513549	-5.9281905	1.8832160
C	-4.3479616	-4.8234097	-1.0146209
H	-2.5649633	-4.1089642	-1.9659706
C	-4.8865904	-5.4579502	0.0958142
H	-4.4770384	-6.3550996	2.0027827
H	-4.9930184	-4.5011071	-1.8237043
H	-5.9544028	-5.6339502	0.1541669
C	-3.2521524	4.3663743	-0.0531819
C	-3.5288869	5.1474594	1.0626159
C	-2.4938491	4.8839109	-1.0969725
C	-3.0485212	6.4476191	1.1314828
H	-4.1082861	4.7406208	1.8832160
C	-2.0032145	6.1771501	-1.0146209
H	-2.2759858	4.2758055	-1.9659706
C	-2.2834283	6.9608865	0.0958142
H	-3.2651585	7.0547788	2.0027827
H	-1.4015639	6.5746343	-1.8237043
H	-1.9019425	7.9736392	0.1541669