Supplementary Informations

In the following, t refers to the number of the transition computed, λ to the transition wavelength (nm) and f to the oscillator strength associated to the t^{th} transition.

PBE0 - vacuum

♯	t	λ	f	ϕ_S	♯	t	λ	f	ϕ_S
1III-c	3	257.53	0.3410	0.65	1III-d	2	275.52	0.4033	0.65
2III-c	2	303.80	0.6996	0.67	2III-d	1	320.74	0.8109	0.69
3III-c	1	349.45	1.0756	0.75	3III-d	1	366.95	1.2081	0.74
4III-c	1	393.40	1.4379	0.78	4III-d	1	411.59	1.5779	0.70
5III-c	1	436.05	1.7712	0.77	5III-d	1	454.89	1.9114	0.72
1V-NH	1	335.46	0.3938	0.70	1V-O	1	334.40	0.3917	0.68
2V-NH	1	431.04	0.4577	0.60	2V-O	1	423.89	0.5479	0.60
3V-NH	1	476.22	0.4524	0.53	3V-O	1	493.14	0.6273	0.53
4V-NH	1	519.82	0.3941	0.41	4V-O	1	545.82	0.6405	0.47
5V-NH	1	548.10	0.3256	0.34	5V-O	1	583.01	0.6194	0.42
1V-S	1	344.11	0.3769	0.71	1V-Se	1	349.77	0.3681	0.72
2V-S	1	443.48	0.5809	0.73	2V-Se	1	456.15	0.5976	0.69
3V-S	1	514.50	0.7077	0.70	3V-Se	1	533.38	0.7864	0.65
4V-S	1	565.16	0.7632	0.62	4V-Se	1	590.26	0.9009	0.58
5V-S	1	598.17	0.7661	0.58	5V-Se	1	631.52	0.9591	0.53
1VI-c	1	322.79	0.4135	0.60					
2VI-c	1	403.83	0.4484	0.49					
3VI-c	1	441.44	0.3540	0.50					
4VI-c	1	455.43	0.2380	0.36					
5VI-c	1	458.86	0.1394	0.23					

PBE0 - acetonitrile

♯	t	λ	f	ϕ_S	♯	t	λ	f	ϕ_S
1III-c	2	279.37	0.4521	0.68	1III-d	2	297.74	0.5020	0.68
2III-c	1	342.82	0.8750	0.69	2III-d	1	359.94	1.0115	0.70
3III-c	1	404.88	1.3215	0.70	3III-d	1	422.26	1.4849	0.70
4III-c	1	464.99	1.7608	0.70	4III-d	1	483.19	1.9448	0.70
5III-c	1	524.20	2.1727	0.69	5III-d	1	543.14	2.3748	0.70
1V-NH	1	367.37	0.5328	0.75	1V-O	1	366.27	0.5421	0.73
2V-NH	1	501.22	0.6404	0.64	2V-O	1	495.80	0.7366	0.64
3V-NH	1	595.14	0.5776	0.55	3V-O	1	599.09	0.7564	0.54
4V-NH	1	632.40	0.4910	0.42	4V-O	1	664.24	0.6906	0.45
5V-NH	1	660.38	0.4093	0.40	5V-O	1	696.47	0.6121	0.38
1V-S	1	376.21	0.5277	0.74	1V-Se	1	380.98	0.5162	0.75
2V-S	1	515.79	0.8093	0.68	2V-Se	1	527.16	0.8396	0.70
3V-S	1	624.27	0.9160	0.65	3V-Se	1	645.22	1.0374	0.64
4V-S	1	688.36	0.8860	0.58	4V-Se	1	728.27	1.1002	0.57
5V-S	1	713.98	0.8169	0.49	5V-Se	1	772.66	1.0995	0.51
1VI-c	1	364.81	0.5528	0.62					
2VI-c	1	481.69	0.5725	0.57					
3VI-c	1	519.15	0.3910	0.40					
4VI-c	1	519.26	0.2424	0.24					
5VI-c	1	509.80	0.1363	0.17					

B3LYP - vacuum

♯	t	λ	f	ϕ_S	♯	t	λ	f	ϕ_S
1III-c	3	263.71	0.3260	0.65	1III-d	2	282.14	0.3905	0.64
2III-c	2	311.41	0.6656	0.66	2III-d	1	328.68	0.7747	0.69
3III-c	1	358.69	1.0162	0.74	3III-d	1	376.42	1.1469	0.73
4III-c	1	404.44	1.3486	0.78	4III-d	1	422.82	1.4876	0.69
5III-c	1	449.18	1.6475	0.76	5III-d	1	468.22	1.7877	0.71
1V-NH	1	344.31	0.3812	0.69	1V-O	1	343.18	0.3796	0.69
2V-NH	1	452.38	0.4217	0.59	2V-O	1	441.88	0.5082	0.59
3V-NH	1	512.28	0.3905	0.51	3V-O	1	523.71	0.5508	0.50
4V-NH	1	571.66	0.3213	0.38	4V-O	1	590.90	0.5291	0.43
5V-NH	1	613.69	0.2506	0.30	5V-O	1	642.41	0.4786	0.37
1V-S	1	353.29	0.3660	0.71	1V-Se	1	358.75	0.3572	0.72
2V-S	1	461.89	0.5462	0.72	2V-Se	1	473.37	0.5660	0.67
3V-S	1	546.17	0.6300	0.69	3V-Se	1	562.34	0.7120	0.63
4V-S	1	611.71	0.6357	0.59	4V-Se	1	633.28	0.7691	0.54
5V-S	1	658.98	0.5912	0.54	5V-Se	1	688.99	0.7659	0.47
1VI-c	1	335.50	0.3890	0.59					
2VI-c	1	432.19	0.3959	0.46					
3VI-c	1	485.48	0.2861	0.46					
4VI-c	1	509.76	0.1738	0.30					
5VI-c	1	518.95	0.0923	0.19					

B3LYP - acetonitrile

♯	t	λ	f	ϕ_S	♯	t	λ	f	ϕ_S
1III-c	2	285.17	0.4385	0.68	1III-d	2	303.95	0.5264	0.68
2III-c	1	349.57	0.8489	0.69	2III-d	1	366.69	0.9835	0.70
3III-c	1	412.60	1.2813	0.69	3III-d	1	429.67	1.4438	0.70
4III-c	1	473.85	1.7053	0.69	4III-d	1	491.38	1.8910	0.70
5III-c	1	534.59	2.1000	0.69	5III-d	1	552.46	2.3063	0.70
1V-NH	1	375.37	0.5190	0.75	1V-O	1	373.72	0.5303	0.75
2V-NH	1	523.73	0.6075	0.64	2V-O	1	513.83	0.7039	0.64
3V-NH	1	645.82	0.5263	0.53	3V-O	1	639.51	0.6948	0.53
4V-NH	1	708.76	0.4239	0.41	4V-O	1	733.64	0.6012	0.43
5V-NH	1	757.68	0.3347	0.38	5V-O	1	790.95	0.4984	0.35
1V-S	1	384.52	0.5154	0.74	1V-Se	1	389.26	0.5020	0.75
2V-S	1	534.12	0.7792	0.67	2V-Se	1	543.63	0.8097	0.70
3V-S	1	664.59	0.8488	0.64	3V-Se	1	679.86	0.9714	0.63
4V-S	1	758.72	0.7704	0.57	4V-Se	1	790.21	0.9795	0.54
5V-S	1	809.81	0.6543	0.45	5V-Se	1	862.73	0.9110	0.46
1VI-c	1	379.03	0.5277	0.62					
2VI-c	1	521.72	0.5231	0.55					
3VI-c	1	586.24	0.3293	0.38					
4VI-c	1	597.80	0.1846	0.21					
5VI-c	1	591.58	0.0940	0.14					

CAM-B3LYP - vacuum

♯	t	λ	f	ϕ_S	♯	t	λ	f	ϕ_S
1III-c	3	254.57	0.3542	0.66	1III-d	2	270.73	0.4147	0.66
2III-c	2	295.17	0.7504	0.71	2III-d	1	310.67	0.8612	0.71
3III-c	1	334.19	1.1902	0.78	3III-d	1	350.53	1.3199	0.76
4III-c	1	370.53	1.6348	0.81	4III-d	1	387.47	1.7711	0.76
5III-c	1	404.17	2.0679	0.82	5III-d	1	421.44	2.2045	0.77
1V-NH	1	325.50	0.4162	0.70	1V-O	1	322.58	0.4097	0.70
2V-NH	1	380.49	0.6003	0.68	2V-O	1	381.30	0.6702	0.69
3V-NH	1	386.97	0.8070	0.70	3V-O	1	412.29	0.9616	0.70
4V-NH	1	394.36	1.0031	0.66	4V-O	1	428.54	1.2890	0.72
5V-NH	1	396.47	1.2131	0.67	5V-O	1	437.28	1.6671	0.75
1V-S	1	332.91	0.3914	0.72	1V-Se	1	339.88	0.3810	0.73
2V-S	1	403.49	0.6650	0.80	2V-Se	1	420.71	0.6614	0.75
3V-S	1	435.85	0.9791	0.82	3V-Se	1	462.19	1.0010	0.76
4V-S	1	451.29	1.3369	0.81	4V-Se	1	483.29	1.3753	0.77
5V-S	1	458.22	1.7368	0.82	5V-Se	1	495.14	1.7902	0.78
1VI-c	5	240.86	0.0299	0.32					
2VI-c	3	275.54	0.0276	0.80					
3VI-c	3	275.93	0.0252	0.80					
4VI-c	3	279.66	0.0526	0.81					
5VI-c	1	316.93	2.0864	0.79					

CAM-B3LYP - acetonitrile

♯	t	λ	f	ϕ_S	♯	t	λ	f	ϕ_S
1III-c	2	281.51	0.4574	0.68	1III-d	1	298.32	0.5496	0.68
2III-c	1	343.53	0.8949	0.70	2III-d	1	360.30	1.0245	0.71
3III-c	1	403.44	1.3663	0.71	3III-d	1	422.06	1.5177	0.72
4III-c	1	459.90	1.8353	0.72	4III-d	1	481.35	2.0012	0.72
5III-c	1	512.51	2.2854	0.73	5III-d	1	537.19	2.4603	0.73
1V-NH	1	364.12	0.5627	0.75	1V-O	1	363.47	0.5589	0.73
2V-NH	1	450.37	0.7733	0.69	2V-O	1	456.63	0.8290	0.69
3V-NH	1	466.20	0.9196	0.66	3V-O	1	486.87	1.0464	0.67
4V-NH	1	458.18	1.0781	0.65	4V-O	1	486.23	1.3054	0.68
5V-NH	1	456.29	1.2429	0.65	5V-O	1	480.72	1.6499	0.71
1V-S	1	372.52	0.5465	0.74	1V-Se	1	378.59	0.5373	0.75
2V-S	1	480.80	0.8778	0.72	2V-Se	1	501.34	0.8954	0.74
3V-S	1	520.10	1.1635	0.75	3V-Se	1	558.24	1.2281	0.73
4V-S	1	518.73	1.4858	0.78	4V-Se	1	572.34	1.5801	0.74
5V-S	1	510.11	1.8984	0.79	5V-Se	1	570.72	2.0025	0.77
1VI-c	1	340.31	0.6089	0.65					
2VI-c	1	380.42	0.8272	0.67					
3VI-c	1	361.15	1.0364	0.63					
4VI-c	1	344.51	1.4957	0.69					
5VI-c	1	335.46	2.1689	0.76					

The ϕ_S index derived from detachment/attachment and NTO's density matrices and one-couple NTOs densities

The IV set of molecules (*Figure 2*) was originally investigated in ref [44] with a different approach. For the sake of consistency, the nomenclature from [44] will be kept in the following table. No confusion must be made with respect to the nomenclature previously used throughout this manuscript: the core of each molecule in the following table is the thieno[3,4-b]pyrazine (molecule IV in the *Figure 2* of the present report), but the investigated derivatives of IV were labelled differently in [44].

♯	t	ϕ_S	$\phi_S^{'}$	ϕ_S^{NTO}	♯	t	ϕ_S	$\phi_S^{'}$	ϕ_S^{NTO}
II-a	1	0.73	0.70	0.72	VI-e	1	0.72	0.69	0.72
II-a	5	0.80	0.78	0.80	VI-f	1	0.74	0.70	0.73
II-a	6	0.39	0.38	0.39	VI-h	1	0.76	0.73	0.75
II-c	1	0.73	0.70	0.72	VI-i	1	0.77	0.74	0.76
II-d	1	0.74	0.71	0.73	VI-n	1	0.70	0.68	0.69
II-e	2	0.76	0.73	0.75	VI-o	1	0.79	0.76	0.78
II-f	1	0.74	0.71	0.73	VI-p	1	0.69	0.66	0.68
II-g	1	0.67	0.64	0.66	VI-q	1	0.80	0.78	0.80
II-i	1	0.72	0.69	0.71	VI-s	1	0.73	0.69	0.72
VI-a	1	0.74	0.72	0.74	VI-t	1	0.72	0.68	0.71
VI-b	1	0.77	0.72	0.76	VI-u	1	0.70	0.67	0.69
VI-d	1	0.71	0.68	0.71	VI-v	1	0.71	0.68	0.70
					VIII	2	0.54	0.53	0.54

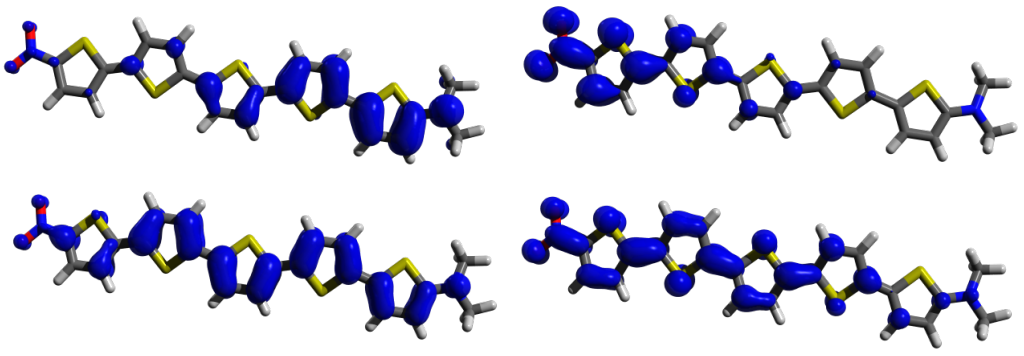

Figure S1 – Qualitative comparison of the charge-transfer character of the 5V-S molecule's first transition, computed in acetonitrile with B3LYP (top) and CAM-B3LYP (bottom). Left part is the detachment density plot in 3D space, while the right part is the attachment density (isodensity 10^{-3}).