Electronic and optical properties of the Spiro-MeOTAD hole conductor in its neutral and oxidized forms: a DFT/TDDFT investigation

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Supporting Information

Table S1. Molecular orbital energies of **1**, $\mathbf{1}^{+}$, $\mathbf{1}^{2+}$ and $\mathbf{1}^{4+}$ in vacuo.

	Spiro-MeOTAD	Spiro-MeOTAD^{+}		Spiro-MeOTAD^{2+}		Spiro-MeOTAD^{4+}	
		α	β	α	β		
L+7 (331)	+0.101	-1.962	-1.923	-3.951	-3.881	-8.090	L+7 (329)
L+6 (330)	+0.076	-1.973	-1.933	-3.964	-3.894	-8.337	L+6 (328)
L+5 (329)	-0.201	-2.201	-2.171	-4.201	-4.137	-8.706	L+5 (327)
L+4 (328)	-0.279	-2.313	-2.276	-4.365	-4.269	-8.722	L+4 (326)
L+3 (327)	-0.357	-2.506	-2.459	-4.669	-4.567	-9.153	L+3 (325)
L+2 (326)	-0.406	-2.545	-2.499	-4.678	-4.580	-9.203	L+2 (324)
L+1 (325)	-0.647	-2.864	-2.797	-5.036	-4.898	-11.673	L+1 (323)
L (324)	-0.672	-2.894	-2.830	-5.066	-4.929	-11.692	L (322)
H (323)	-4.264 (323)	-6.412 (O)	-5.722 (V)	-8.526 O	-7.556 V	-12.450 (321)	H (321)
H-1 (322)	-4.291	-6.435	-6.143	-8.544 O	-7.581	-12.461	H-1 (320)
H-2 (321)	-4.727	-6.880	-6.650	-8.961	-8.529	-13.442	H-2 (319)
H-3 (320)	-4.734	-6.887	-6.651	-8.970	-8.542	-13.444	H-3 (318)
H-4 (319)	-5.731	-7.862	-7.740	-9.799	-9.643	-13.454	H-4 (317)
H-5 (318)	-5.961	-7.910	-7.856	-9.802	-9.676	-13.457	H-5 (316)
H-6 (317)	-5.989	-7.911	-7.862	-9.811	-9.705	-13.692	H-6 (315)
H-7 (316)	-5.999	-7.915	-7.867	-9.814	-9.708	-13.800	H-7 (314)
H-8 (315)	-5.999	-7.920	-7.870	-9.893	-9.731	-14.413	H-8 (313)
H-9 (314)	-6.006	-8.023	-7.933	-10.004	-9.815	-14.414	H-9 (312)

Table S2. Molecular orbital energies of **1**, $\mathbf{1}^{+}$, $\mathbf{1}^{2+}$ and $\mathbf{1}^{4+}$ in ethanol.

	Spiro-MeOTAD	Spiro-MeOTAD^{+}		Spiro-MeOTAD^{2+}		Spiro-MeOTAD^{4+}	
		α	β	α	β		
L+7 (331)	-0.053	-0.393	-0.352	-0.701	-0.626	-1.482	L+7 (329)
L+6 (330)	-0.077	-0.411	-0.369	-0.719	-0.644	-1.660	L+6 (328)
L+5 (329)	-0.350	-0.651	-0.622	-0.947	-0.887	-1.994	L+5 (327)
L+4 (328)	-0.430	-0.744	-0.711	-1.065	-0.980	-2.012	L+4 (326)
L+3 (327)	-0.509	-0.900	-0.854	-1.322	-1.220	-2.481	L+3 (325)
L2 (326)	-0.560	-0.940	-0.896	-1.330	-1.232	2.532	+2 (324)
L+1 (325)	-0.802	-1.252	-1.183	-1.704	-1.551	-5.104	L+1 (323)
L (324)	-0.828	-1.282	-1.215	-1.736	-1.583	-5.132	L (322)
H (323)	-4.418 (323)	-4.843 (O)	-4.141 V	-5.269O	-4.265 V	-5.970 (321)	H (321)
H-1 (322)	-4.447	-4.868	-4.572	-5.293	-4.297V	-5.982	H-1 (320)
H-2 (321)	-4.883	-5.338	-5.108	-5.753	-5.320	-7.058	H-2 (319)
H-3 (320)	-4.890	-5.344	-5.108	-5.763	-5.333	-7.059	H-3 (318)
H-4 (319)	-5.893	-6.295	-6.171	-6.637	-6.426	-7.065	H-4 (317)
H-5 (318)	-6.112	-6.407	-6.339	-6.664	-6.530	-7.068	H-5 (316)
H-6 (317)	-6.146	-6.413	-6.368	-6.668	-6.579	-7.129	H-6 (315)
H-7 (316)	-6.149	-6.417	-6.374	-6.668	-6.581	-7.242	H-7 (314)
H-8 (315)	-6.157	-6.423	-6.378	-6.672	-6.585	-7.891	H-8 (313)
H-9 (314)	-6.168	-6.470	-6.397	-6.759	-6.600	-7.892	H-9 (312)

Table S3. Energy, wavelength, oscillator strength, and composition of the TDDFT excitations of **1** in vacuo. For the closed shell **1** we report the percentage of each electronic excitation composing the TDDFT eigenvectors.

States	Energy (eV)	Wavelength (nm)	F	Composition
1	3.115	398	0.57	86% (323 -> 324); 6% (322 -> 325)
2	3.169	391	0.87	75% (323 -> 325); 15% (322 -> 324)
3	3.179	390	0.11	39% (322 -> 324); 19% (323 -> 325)
4	3.197	388	0.19	88% (322 -> 325); 9% (323 -> 324)
5	3.336	372	0.06	73% (323 -> 326); 19% (322 -> 327)
17	3.826	324	0.07	40% (323 -> 331); 27% (322 -> 330); 7% (322 -> 335); 7% (320 -> 328); 6% (323 -> 333)
21	3.936	315	0.28	47% (323 -> 333); 24% (322 -> 330); 15% (322 -> 335)
22	3.936	315	0.38	48% (323 -> 332); 24% (322 -> 334); 14% (321 -> 327)
23	3.941	315	0.07	42% (323 -> 330); 26% (322 -> 333); 14% (323 -> 335); 6% (322 -> 331)
25	3.957	313	0.06	54% (321 -> 327); 18% (320 -> 326); 9% (323 -> 332); 6% (323 -> 336)
26	3.960	313	0.05	46% (323 -> 331); 29% (322 -> 330); 8% (323 -> 337); 7% (322 -> 335)

Table S4. Energy, wavelength, oscillator strength, and composition of the TDDFT excitations of $\mathbf{1}^+$ in vacuo. For the open shell $\mathbf{1}^+$ we report the coefficient of each electronic excitation composing the TDDFT eigenvectors.

States	Energy (eV)	Wavelength (nm)	f	Composition
2	0.687	1806	0.24	0.80 (321β -> 323β) ; 0.37 (320β-> 323β)
3	0.716	1731	0.26	0.80 (320β -> 323β) ; -0.36(321β -> 323β)
5	1.753	707	0.02	0.82 (318β -> 323β) ; 0.54 (314β -> 323β)
6	1.774	699	0.06	0.99 (316β -> 323β)
9	1.795	690	0.08	0.83 (314β -> 323β) ; -0.54 (318β -> 323β)
18	2.480	500	0.01	0.63 (322β->325β) ; 0.46 (323α->324α) ; -0.42 (322α->325α) ; 0.33 (305β ->323β) ; -0.31 (311β -> 323β)
27	2.977	417	0.24	0.58 (322β->327β) ; 0.46 (322β->325β) ; -0.36 (323α->324α) ; -0.36 (323α -> 326α) ; -0.29 (322α -> 327α)
28	3.001	413	0.41	0.49 (322β->327β) ; 0.49 (323α->324α) ; -0.48 (322β->325β)
29	3.004	413	0.79	0.62 (322β->324β) ; 0.48 (322α->324α) ; -0.49 (323α->325α)

Table S5. Energy, wavelength, oscillator strength, and composition of the TDDFT excitations of $\mathbf{1}^{2+}$ in vacuo. For the open shell $\mathbf{1}^{2+}$ we report the coefficient of each electronic excitation composing the TDDFT eigenvectors.

States	Energy (eV)	Wavelength (nm)	f	Composition
5	1.641	756	0.02	0.86(319β->322β); 0.33(315β->322β); -0.28(318β->323β)
8	1.740	713	0.07	0.77(316β->322β) ; 0.60(317β->323β)
9	1.741	712	0.17	0.73(315β->322β) ; 0.64(318β->323β)
10	1.747	710	0.02	0.81(317β->322β) ; 0.53(316β->323β)
16	1.849	671	0.03	0.95(314β->323β) ; -0.22(318β->323β)
23	2.449	506	0.04	0.74(309β->322β) ; -0.59(308β->323β)
24	2.452	506	0.05	0.69(308β->322β) ; -0.65(309β->323β)
37	2.726	455	0.42	0.65(323α->324α) ; -0.51(322α->325α) ; -0.27(306β->323β) ; 0.24(305β->322β)
38	2.74 0	453	0.40	0.57(322α->324α) ; -0.56(323α->325Aα ; 0.30(305β->323β) ; -0.27(306β -> 322β)
39	2.757	450	0.09	0.62(305β->323β) ; -0.58(306β->322β) ; -0.27(301β->323β) ; 0.27(323α->325α) ; 0.27(322α -> 324α)
40	2.762	449	0.08	0.68(306β->323β); -0.52(305β->322β) ; 0.35(301β -> 322β) ; 0.26(323α->324α)

Table S6. Energy, wavelength, oscillator strength, and composition of the TDDFT excitations of $\mathbf{1}^{4+}$ in vacuo. For the closed shell $\mathbf{1}^{4+}$ we report the percentage of each electronic excitation composing the TDDFT eigenvectors.

States	Energy (eV)	Wavelength (nm)	F	Character
3	1.196	1037	1.37	18%(320->322); 17%(321->323)
4	1.204	1030	1.15	19%(320->323); 17%(321->322)
11	1.721	721	0.26	39%(317 -> 323); 36%(316 -> 322)
13	1.734	715	0.59	39%(318->323); 36%(319->322)
14	1.740	712	0.07	39%(316 -> 323); 36%(317 -> 322)
25	2.481	500	0.03	70%(309 -> 322); 27%(306 -> 323)
58	3.668	338	0.02	93%(320 -> 328)
64	3.836	323	0.03	72%(318 -> 324); 22%(319 -> 325)
66	3.844	323	0.09	72%(316 -> 324); 23%(317 -> 325)
80	3.964	313	0.02	91%(320 -> 329)
85	4.045	307	0.04	86%(315 -> 324)
86	4.086	304	0.01	46%(315 -> 325)+30%(289 -> 322)+12%(288 -> 323)
91	4.185	296	0.17	60%(314->324)+ 15%(321->330)
92	4.218	294	0.08	49%(314->325)+30%(320 -> 330)
95	4.234	293	0.01	53%(284->322)+26%(285->323)
97	4.255	291	0.08	51%(321 -> 331) +34%(320 -> 332)

Figure S1: Simulated absorption spectrum of $\mathbf{1}^{+}$ in vacuo (green line) and ethanol solution (red line).