Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry

Chiroptical, Linear, and Second-order Nonlinear Optical Properties of Binaphthol Derivatives

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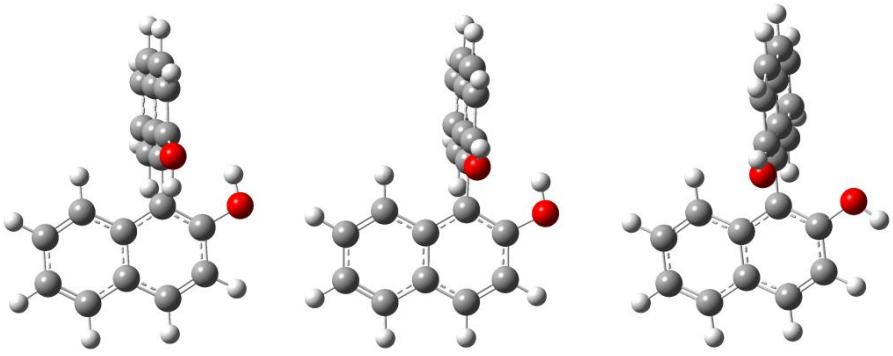


1a **1b** **1c**

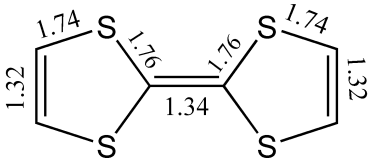
Figure S1. Optimized geometries of the three most stable conformers of **1** at the B3LYP/cc-pVDZ level of theory.

TABLE S1. The relative Gibbs free energies ΔG (kcal/mol), relative total energies ΔE (kcal/mol), and the normalized Boltzmann factor B_f (in %) at 298.15 K based on the relative Gibbs free energy and the relative total energy of the conformers of **1** at the B3LYP/cc-pVDZ level of theory.

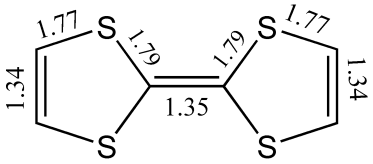
Conformer	ΔE	$B_f(\Delta E)$	ΔG	$B_f(\Delta G)$
1a	0	99.83	0	99.82
1b	3.77	0.17	3.74	0.18
1c	6.88	0	6.67	0.

TABLE S2. The relative Gibbs free energies ΔG (kcal/mol), relative total energies ΔE (kcal/mol), and the normalized Boltzmann factor B_f (in %) at 298.15 K based on the relative Gibbs free energy and the relative total energy of the conformers of **2** at the B3LYP/cc-pVDZ level of theory.

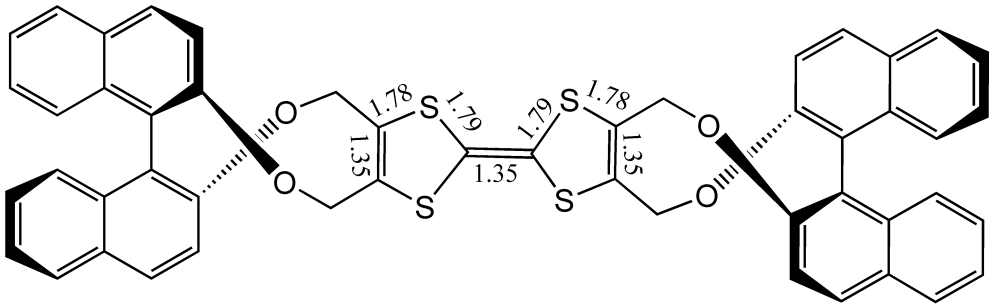
Conformer	ΔE	$B_f(\Delta E)$	ΔG	$B_f(\Delta G)$
Boat	0	63.32	0	66.92
Chair	0.32	36.68	0.42	33.08



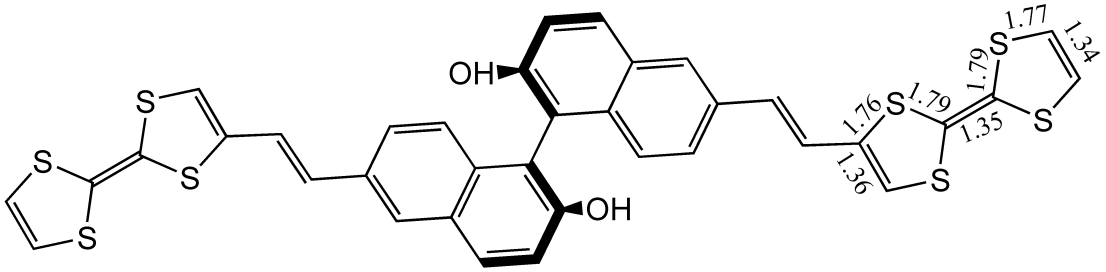
Experimental TTF monomer structrue



Calculated TTF monomer structrue



TTF structrue in System 5



TTF structrue in System 6

Figure S2. Main TTF structural parameters in monomer and in the derivatives **5** and **6.**

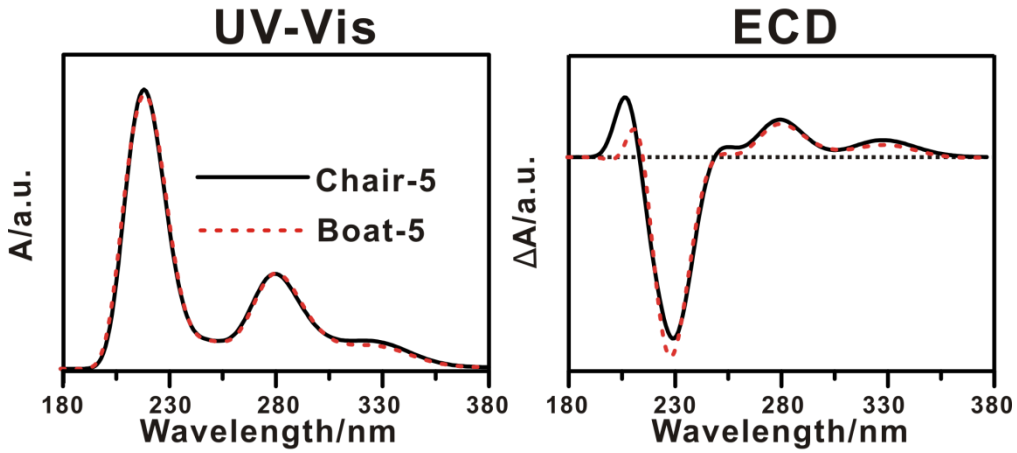


Figure S3. The simulated UV spectra (left) and CD spectra (right) of the two most stable conformers (Chair and Boat).

Table S3. The Calculated excitation energies, oscillator strengths and rotational strengths for the neutral state in the gas phase at the B3LYP/cc-pVDZ level of theory of compound **1**.

states	eV	λ[a]	*f*[b]	Rlength[c]	Rvelocity[c]
1	3.8932	318.46	0.0190	-8.7862	-8.2847
2	3.9016	317.77	0.0000	0.0454	-0.1009
3	4.0521	305.98	0.1237	-16.5915	-18.8448
4	4.0801	303.88	0.0152	66.6196	72.0004
5	4.4718	277.26	0.0431	-12.3791	-13.2966
6	4.4822	276.61	0.0010	2.3183	2.5715
7	4.6742	265.25	0.0025	0.8466	0.7596
8	4.6743	265.24	0.0005	1.8359	1.4438
9	4.8798	254.08	0.0016	-0.9165	-1.2598
10	4.8834	253.89	0.0077	-4.2222	-5.3101
11	5.4591	227.11	0.3301	-515.5974	-525.8279
12	5.5170	224.73	0.1108	260.7425	267.4812
13	5.6047	221.21	0.0323	64.8656	64.5669
14	5.6113	220.96	0.0399	-48.9804	-48.2418
15	5.6441	219.67	0.0473	78.7726	76.4788
16	5.6546	219.26	0.1258	-55.7466	-63.2045
17	5.6930	217.78	0.3414	-102.0544	-101.2094
18	5.7624	215.16	0.2325	354.7598	364.7665
19	5.8001	213.76	0.4982	-716.4754	-722.0893
20	5.8586	211.63	0.0830	46.5660	48.4909

21	5.8755	211.02	0.0706	14.8608	15.1932
22	5.8851	210.67	0.2764	300.3366	304.3541
23	6.0944	203.44	0.1397	-305.4308	-308.5138
24	6.1021	203.18	0.2188	503.6558	513.5018
25	6.3439	195.44	0.0026	31.6079	32.0199
26	6.3459	195.38	0.0303	150.7991	150.7149
27	6.4440	192.40	0.0040	0.4266	0.4361
28	6.4494	192.24	0.0002	0.8989	0.4905
29	6.5712	188.68	0.0002	0.7510	0.8855
30	6.5846	188.29	0.0648	22.0554	23.5050
31	6.6047	187.72	0.0326	-25.0129	-26.0675
32	6.6091	187.60	0.0038	-0.1644	-0.1633
33	6.6684	185.93	0.0204	-4.3954	-5.6378
34	6.6921	185.27	0.0083	-14.9169	-19.5794
35	6.7028	184.97	0.0030	-0.8087	-0.8106
36	6.7164	184.60	0.0132	-29.1294	-34.1484
37	6.7949	182.47	0.0001	1.1547	-0.1896
38	6.7959	182.44	0.0001	-0.3643	0.4386
39	6.8124	182.00	0.0114	3.5939	3.7538
40	6.8294	181.54	0.0063	8.4642	8.1603
41	7.0321	176.31	0.0001	-0.3761	-0.5207
42	7.0323	176.31	0.0000	-0.7363	-0.4276
43	7.1301	173.89	0.0179	-2.0860	-2.1806
44	7.1338	173.80	0.0203	8.4555	8.2019
45	7.1517	173.36	0.0111	-5.8624	-5.2582
46	7.1797	172.69	0.0129	5.0653	4.8880
47	7.1927	172.38	0.0016	8.0484	7.0305
48	7.2068	172.04	0.0068	-3.5862	-2.4779
49	7.2841	170.21	0.0015	-5.2395	-6.6992
50	7.3076	169.66	0.0001	0.1758	0.8136
51	7.3566	168.54	0.0074	-28.7742	-19.4103
52	7.3728	168.16	0.0083	-11.1181	-5.0663
53	7.4051	167.43	0.0037	-17.3484	-11.0365
54	7.4068	167.39	0.0052	8.7013	6.2717
55	7.4370	166.71	0.0001	-0.6400	-0.7344
56	7.4488	166.45	0.0002	2.1103	1.7778
57	7.4562	166.28	0.0192	-9.2769	-9.8723
58	7.4833	165.68	0.0366	-4.0598	-3.6535
59	7.4931	165.47	0.0100	21.4211	18.7564
60	7.5249	164.77	0.0049	-4.5310	-4.6113
61	7.5807	163.55	0.0082	9.1994	9.4202
62	7.5916	163.32	0.0000	-0.7642	-0.2600
63	7.5991	163.16	0.0302	-7.9479	-8.1316
64	7.6011	163.11	0.0027	12.7311	12.5987

65	7.6222	162.66	0.0348	-26.3035	-27.1599
66	7.6287	162.52	0.0001	0.1866	0.8604
67	7.6770	161.50	0.0017	6.9069	7.0270
68	7.6805	161.43	0.0081	-7.9766	-8.6129
69	7.7501	159.98	0.0030	-6.7601	-7.6709
70	7.7575	159.83	0.0032	3.1708	3.3650
71	7.7695	159.58	0.0073	11.2275	11.6041
72	7.7720	159.53	0.0018	-12.5539	-8.8399
73	7.8305	158.33	0.0042	-19.4874	-20.9342
74	7.8372	158.20	0.4764	-62.1129	-67.9563
75	7.8472	158.00	0.0792	59.8475	60.8865
76	7.8602	157.74	0.0036	-1.4072	-0.9714
77	7.8628	157.68	0.0005	14.5250	12.8637
78	7.8802	157.34	0.0124	11.5614	11.1501
79	7.8830	157.28	0.1215	-8.0698	-7.2124
80	7.8917	157.11	0.0004	10.7326	6.3269
81	7.9591	155.78	0.0011	3.7044	4.0428
82	7.9624	155.71	0.0001	0.3410	0.2671
83	8.0535	153.95	0.0543	4.5586	5.4994
84	8.0619	153.79	0.0067	-3.7141	-3.8863
85	8.1301	152.50	0.0223	-14.2843	-13.1698
86	8.1354	152.40	0.0004	-0.1109	-0.5866
87	8.1645	151.86	0.0004	-1.1933	-1.4288
88	8.1835	151.50	0.0008	-0.6553	-0.4369
89	8.1840	151.50	0.0025	-4.1980	-3.9450
90	8.2032	151.14	0.0001	2.9850	1.3469
91	8.2052	151.10	0.0192	-3.8067	-2.9098
92	8.2416	150.44	0.0009	1.7755	1.4644
93	8.2504	150.28	0.0262	31.4423	33.0905
94	8.2538	150.21	0.0089	0.4379	0.4284
95	8.2970	149.43	0.0144	5.2568	5.5637
96	8.3030	149.32	0.0016	-1.6931	-2.3720
97	8.3164	149.08	0.2299	-28.2670	-29.4477
98	8.3369	148.72	0.0134	-17.3201	-17.7164
99	8.3768	148.01	0.0000	0.9302	0.4332
100	8.3811	147.93	0.0116	15.8401	14.6714
101	8.4017	147.57	0.0025	-10.5705	-6.4456
102	8.4110	147.41	0.0029	12.1730	8.6729
103	8.4246	147.17	0.0003	-2.7334	-2.3135
104	8.4422	146.86	0.0052	4.0574	2.4465
105	8.4589	146.57	0.0066	-6.5311	-5.4669
106	8.4630	146.50	0.0005	2.6567	7.8003
107	8.4712	146.36	0.0008	5.0293	4.0992
108	8.4739	146.31	0.0026	1.5931	-0.2459

109	8.4946	145.96	0.0016	5.5957	4.1949
110	8.4988	145.88	0.0016	-5.2729	-3.5062
111	8.5113	145.67	0.0005	-2.0831	-1.7396
112	8.5124	145.65	0.0022	-2.6502	-2.8943
113	8.5470	145.06	0.0005	-1.6796	-1.6416
114	8.5639	144.77	0.0001	0.5694	0.8116
115	8.6293	143.68	0.0106	4.9601	5.9738
116	8.6338	143.60	0.0022	3.8194	3.4570
117	8.6536	143.27	0.0294	-24.4791	-24.5309
118	8.6781	142.87	0.0105	-1.2823	-0.9823
119	8.6944	142.60	0.0094	29.9251	27.1671
120	8.6966	142.57	0.0017	-3.0983	-2.0627
121	8.7082	142.38	0.0005	1.1588	3.5971
122	8.7411	141.84	0.0015	0.5013	0.4226
123	8.7437	141.80	0.0054	18.3131	16.9493
124	8.7661	141.44	0.0042	-16.2075	-17.5695
125	8.7699	141.37	0.0013	-3.7169	-3.6215
126	8.7832	141.16	0.0005	-4.0380	-4.1590
127	8.8195	140.58	0.0124	1.2844	1.3514
128	8.8377	140.29	0.0004	-0.9911	-1.3142
129	8.8795	139.63	0.0001	-0.0027	-0.0036
130	8.8859	139.53	0.0001	0.5150	0.5922
131	8.9280	138.87	0.0010	4.9857	3.3143
132	8.9358	138.75	0.0010	-5.6231	-4.3135
133	8.9580	138.41	0.0018	-1.9193	-1.7502
134	8.9644	138.31	0.0000	-0.0685	-0.2098
135	9.0562	136.91	0.0006	0.6604	0.6369
136	9.0587	136.87	0.0001	-0.1378	-0.1077
137	9.0742	136.63	0.0010	1.2163	1.5639
138	9.0938	136.34	0.0018	-13.7176	-13.7034
139	9.0982	136.27	0.0009	2.8326	3.0898
140	9.1165	136.00	0.0211	-3.1015	-2.7490
141	9.1256	135.86	0.0108	4.9770	5.7773
142	9.1332	135.75	0.0084	0.7828	0.7843
143	9.1341	135.74	0.0001	5.5577	4.6381
144	9.1427	135.61	0.0000	-3.2319	-0.0348
145	9.1498	135.50	0.0012	-4.7795	-3.7511
146	9.1524	135.47	0.0056	5.3835	4.4810
147	9.1698	135.21	0.0010	0.7505	-0.2483
148	9.1791	135.07	0.0007	-3.1792	-3.7541
149	9.1917	134.89	0.0005	-0.4880	-0.7285
150	9.1979	134.80	0.0006	-1.0307	-1.3614

[a]λ in nm. [b] Oscillator Strengths. [c] R values (in 10^{-40} esu^2cm^2) using the velocity-gauge representation and length-gauge representation of the electric dipole operator.

Table S4. Calculated Electron Absorption Energy (λ_{cal}, nm), Oscillators Strengths (*f*), Major Contribution, and Experimental Data (λ_{exp}, nm) of compounds **1**-7

Species	λ_{exp}	λ_{cal}	*f*	main contribution
1	230	211	0.2764	HOMO-4→LUMO+1 HOMO-3→LUMO+3
	335	306	0.1237	HOMO→LUMO HOMO-1→LUMO +1
2	208	201	0.3483	HOMO-3→LUMO+3 HOMO-1→LUMO+5
	236	224	0.3476	HOMO-1→LUMO+3 HOMO-2→LUMO+2
	264	273	0.2109	HOMO→LUMO+2 HOMO-5→LUMO
	328	381	0.0838	HOMO→LUMO
3		208	0.3737	HOMO-6→LUMO+3 HOMO-6→LUMO+2
		313	0.2137	HOMO-1→LUMO HOMO-2→LUMO
5		217	0.3952	HOMO-14→LUMO HOMO-15→LUMO+1
		280	0.5263	HOMO→LUMO +12 HOMO→LUMO+13
6		305	0.7311	HOMO-4→LUMO HOMO-5→LUMO +1
		353	1.2558	HOMO-3→LUMO

				HOMO-2→LUMO+1
		496	0.2666	HOMO-1→LUMO HOMO→LUMO+1
7	301	307	0.1162	HOMO-2→LUMO+4 HOMO-3→LUMO+4
	343	355	0.5288	HOMO-10→LUMO+1 HOMO→LUMO+5
	455	469	0.4614	HOMO-2→LUMO+1 HOMO→LUMO+3
		691	0.2308	HOMO→LUMO+1 HOMO-1→LUMO

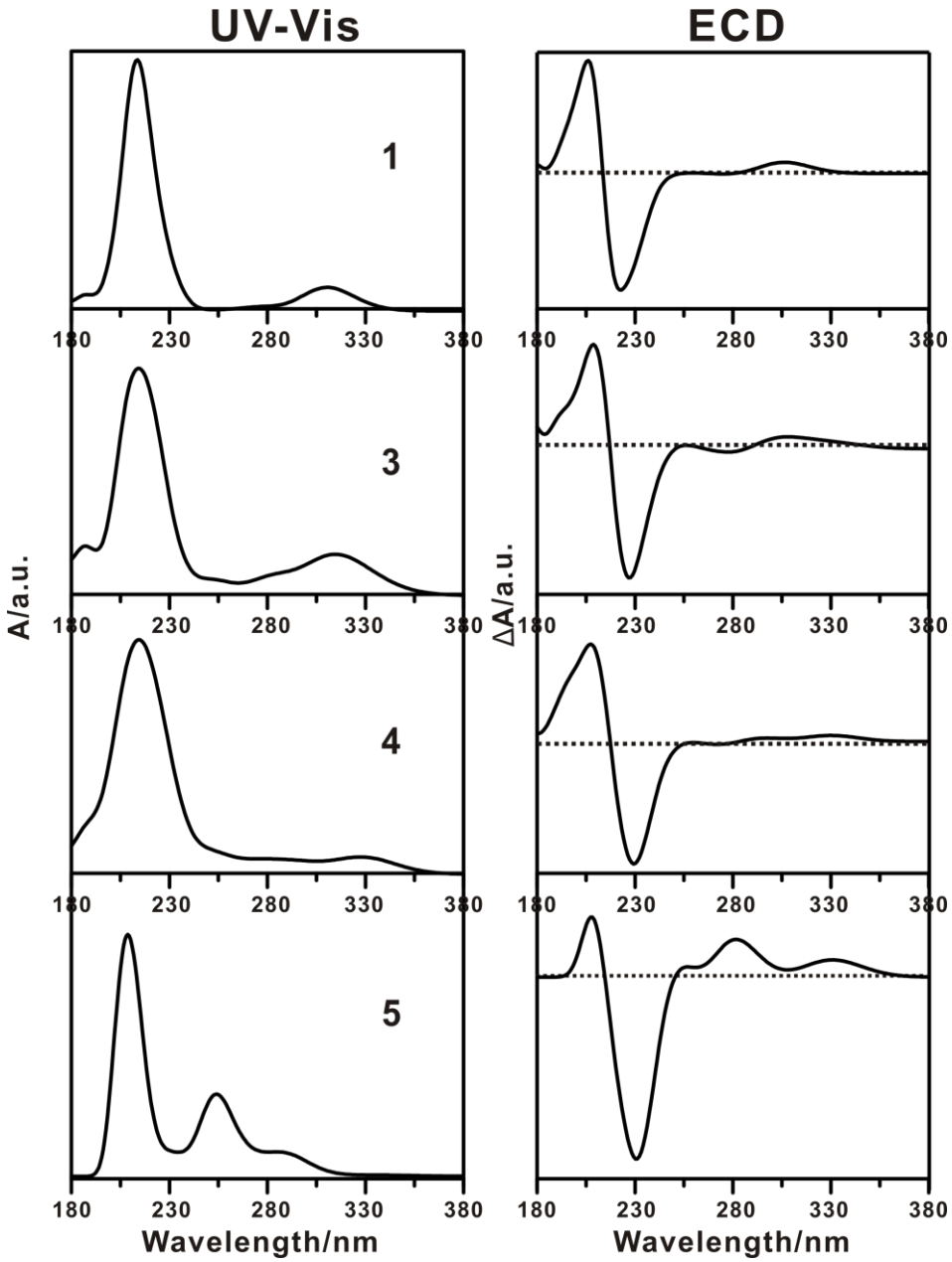
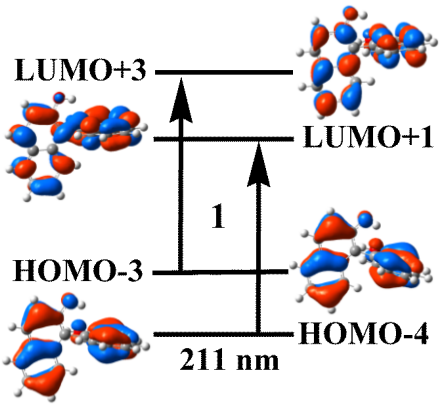
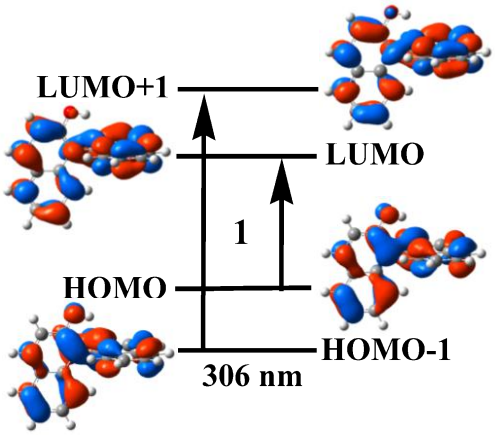
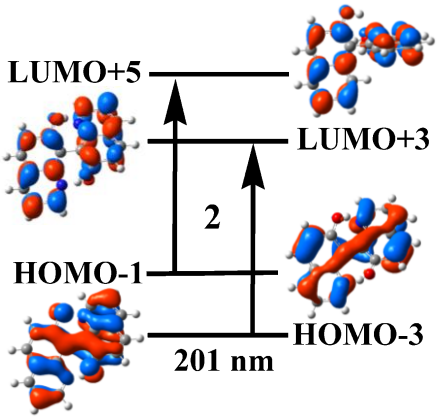
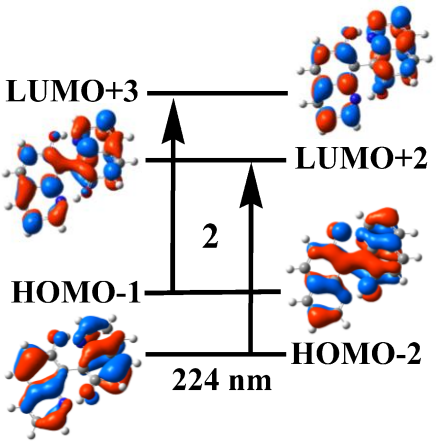


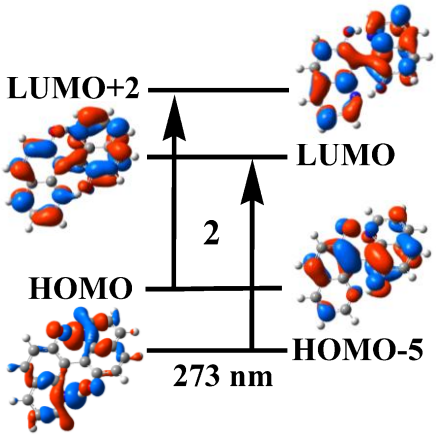
Figure S4. Calculated UV (left) and CD (right) spectra of compounds **1**, **3**, **4** and **5** at the TDB3LYP/cc-pVDZ level of theory.

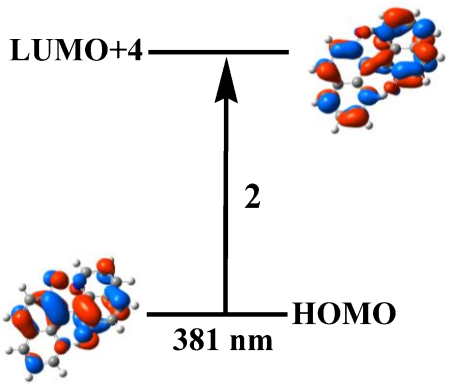


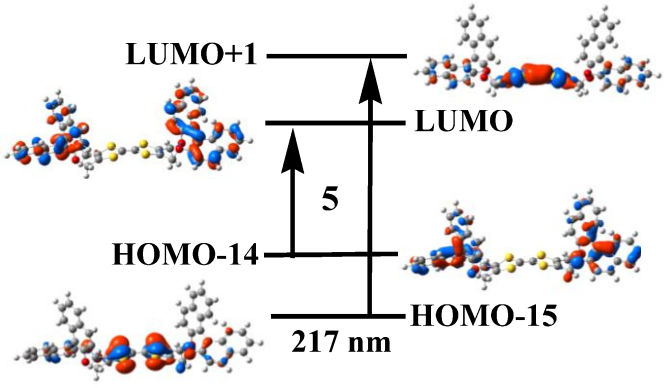


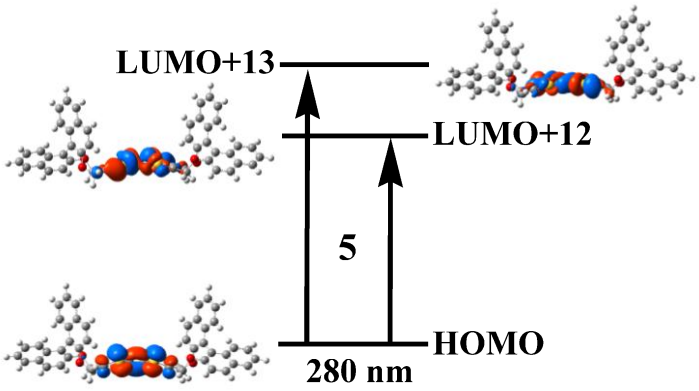


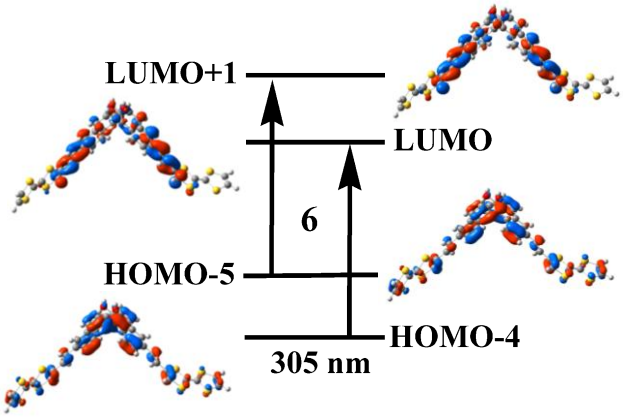


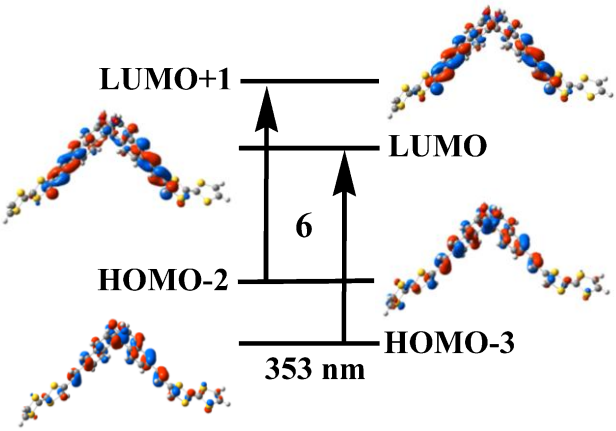


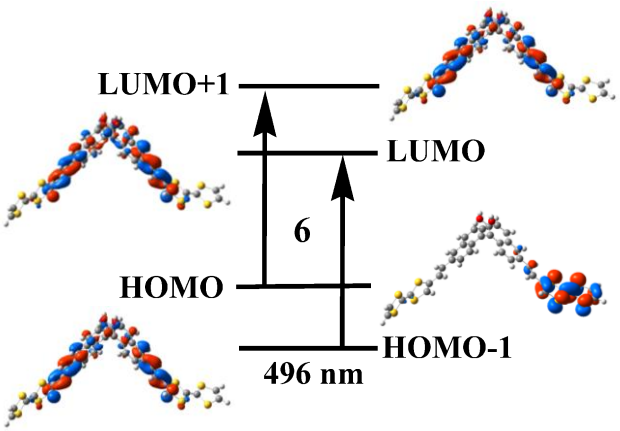


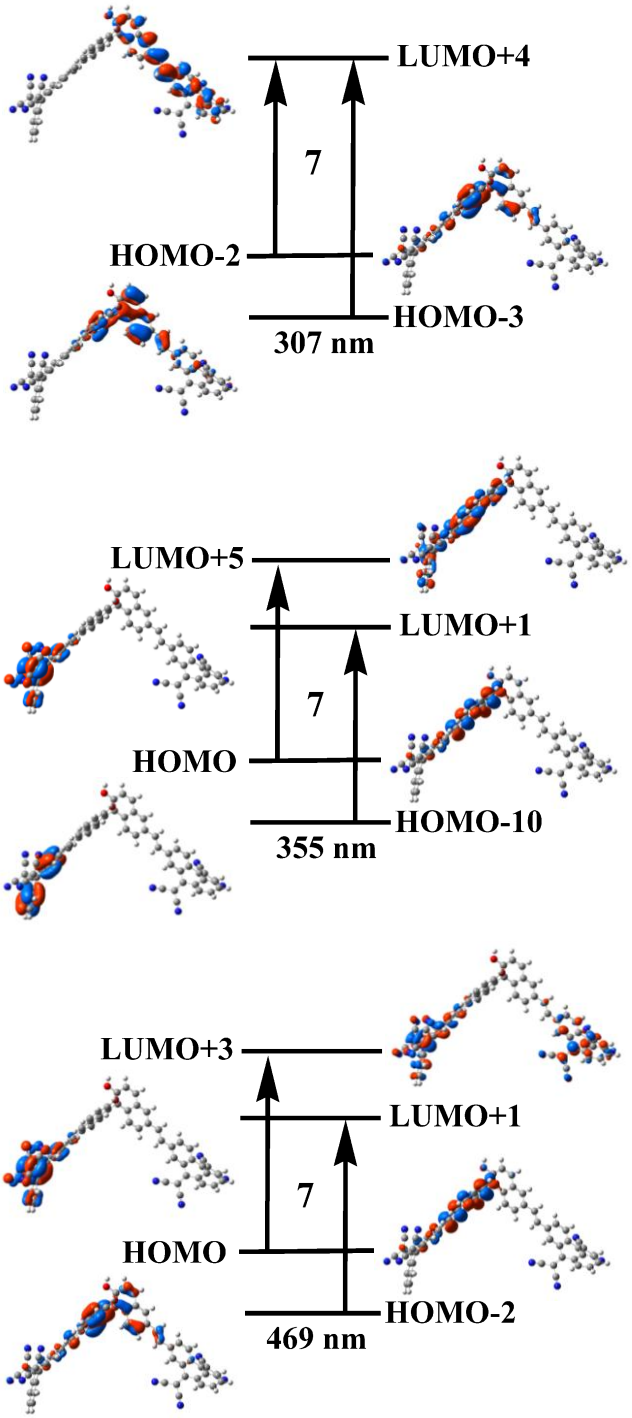












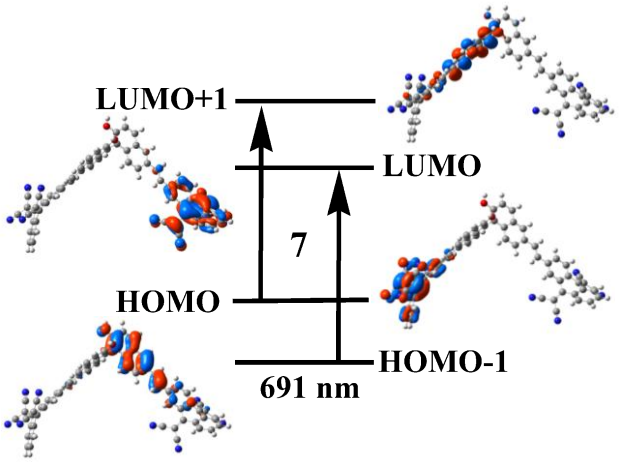


Figure S5. Molecular orbitals involved into the main absorption transition of compounds **1**, 2, **5**-**7**.

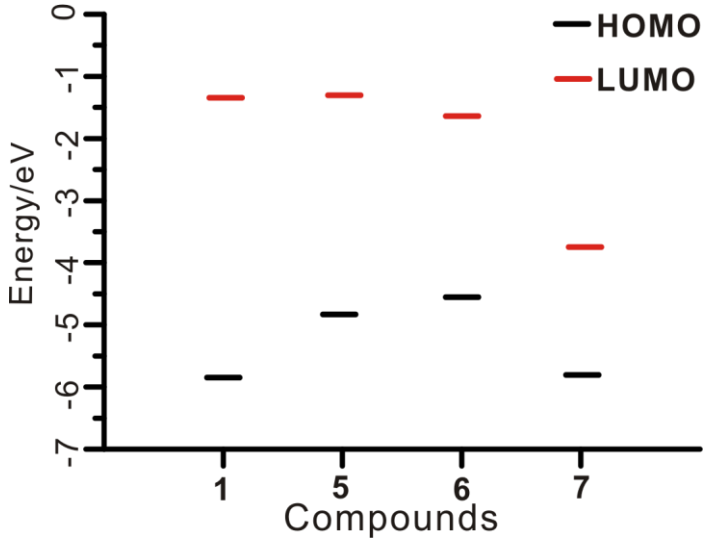
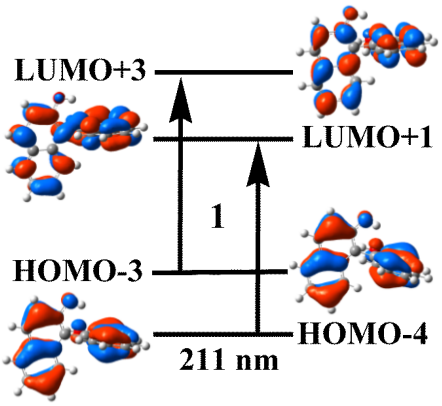
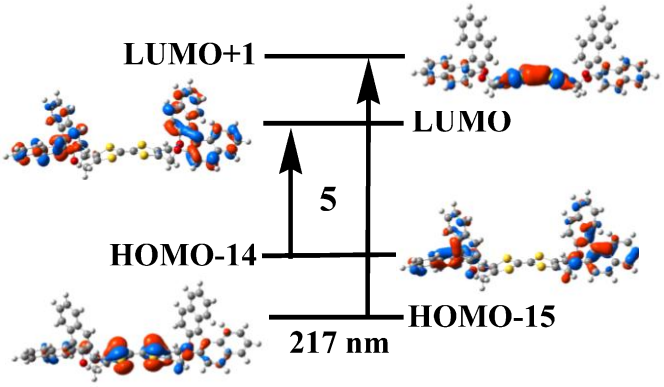
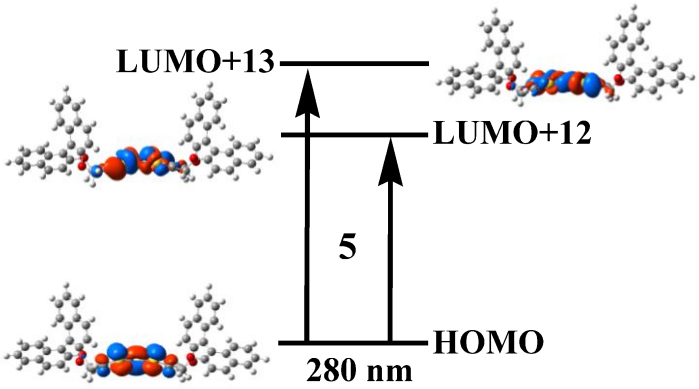
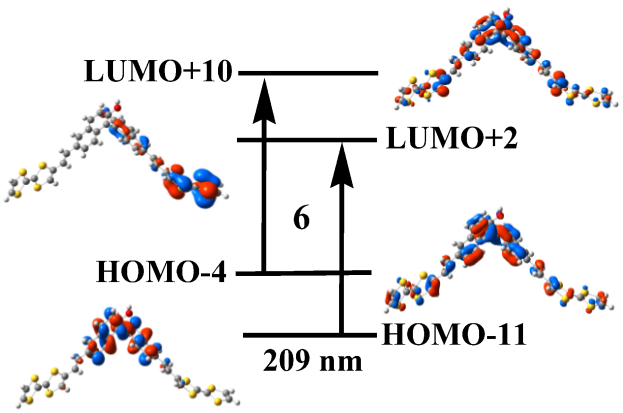


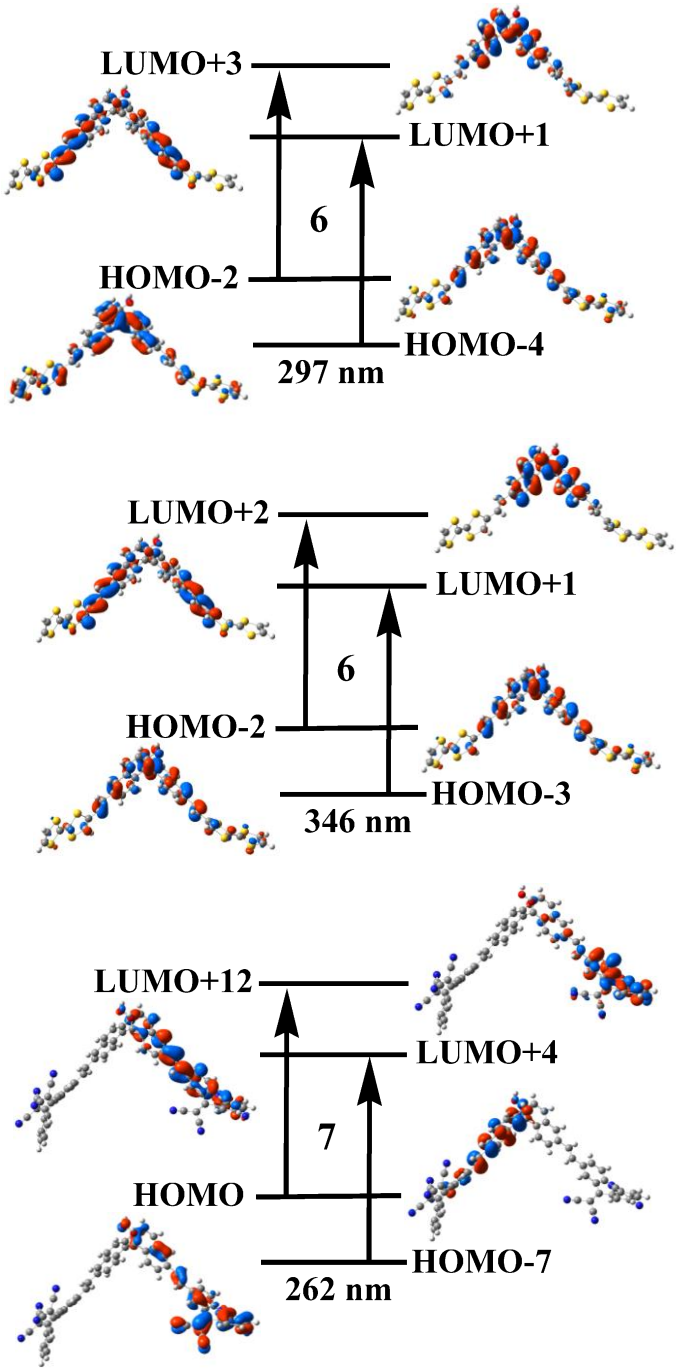
Figure S6. Orbital energy level diagrams of the concerned compounds











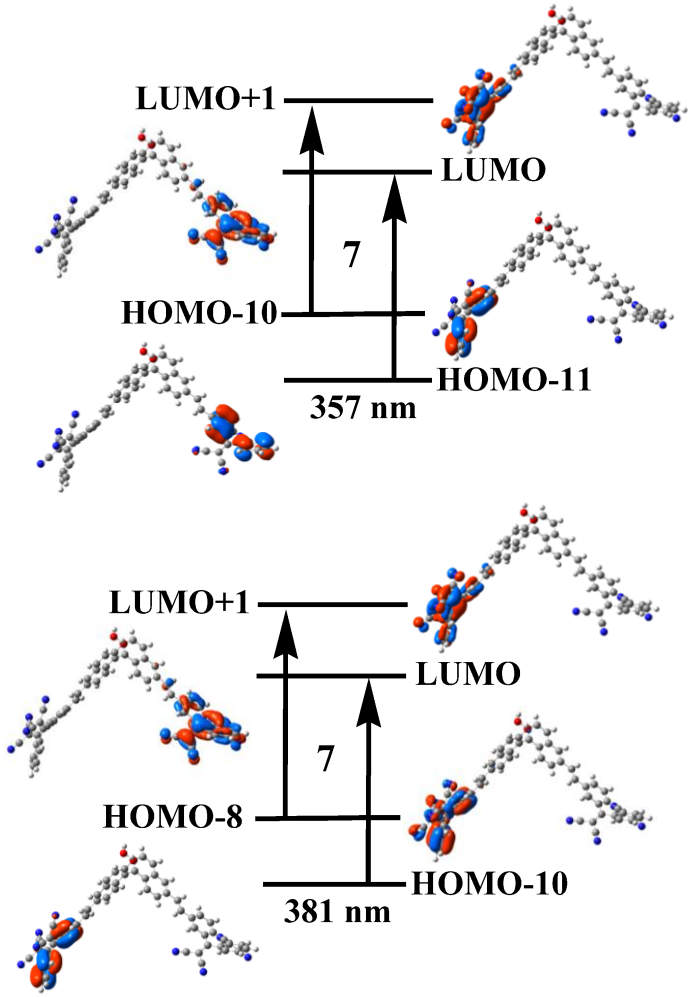
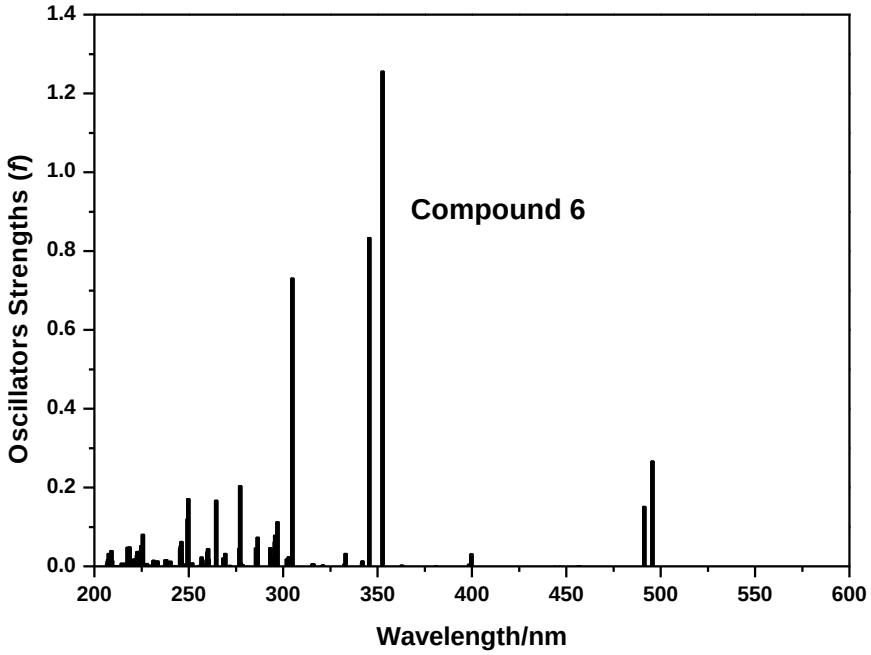
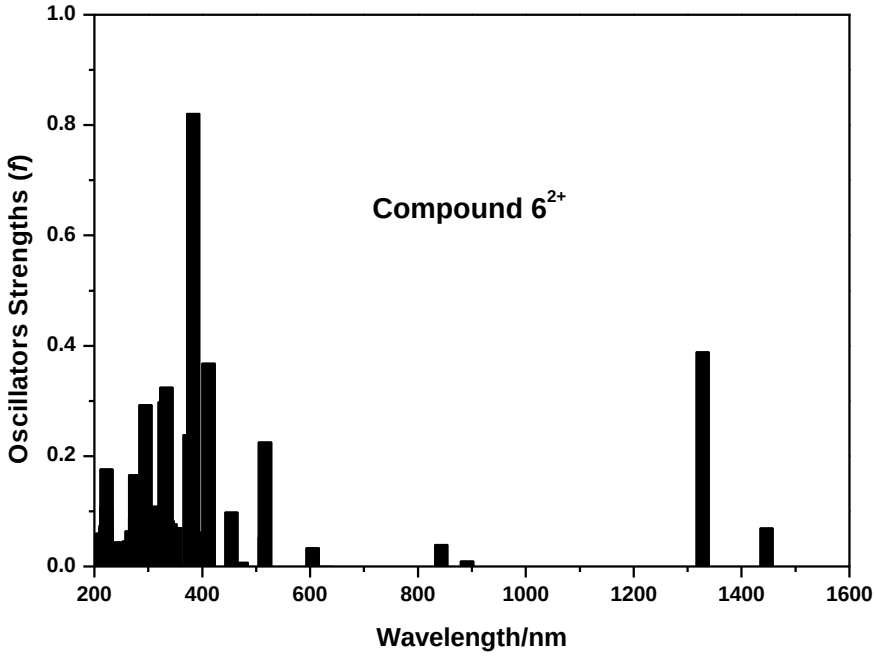


Figure S7. Molecular orbitals involved into the main CD transition of compounds **1** and **5-7**.

Table S4. Calculated OR values at five different excitation wavelengths (589, 578, 546, 436, and 365 nm) of compounds **5-7** at B3LYP/cc-pVTZ level of theory.

Compound	589	578	546	436	365
5	1069.49	1133.71	1360.17	3075.64	8564.14
6	-479.77	-468.44	-223.44	-28476.32	-3383.82
7	-4090.05	-3961.90	-3932.49	-13428.84	-203025.11





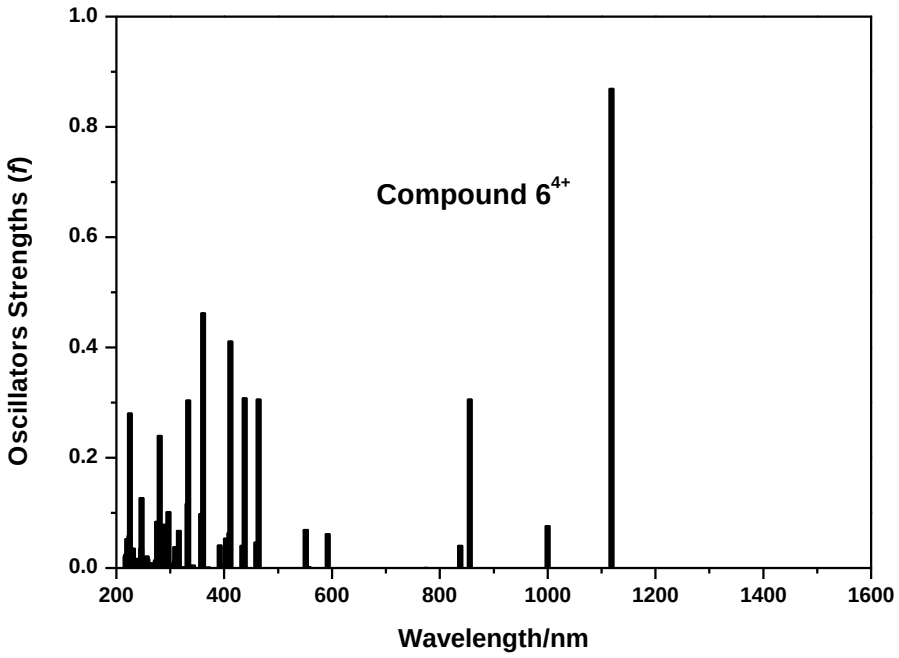


Figure S8. The relationship between excitation wavelength and oscillator strengths for compound **6** and its cations ($\mathbf{6}^{2+}$ and $\mathbf{6}^{4+}$).