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Theoretical study on thiophene-based double helicenes with intrinsic large second-order nonlinear optical response

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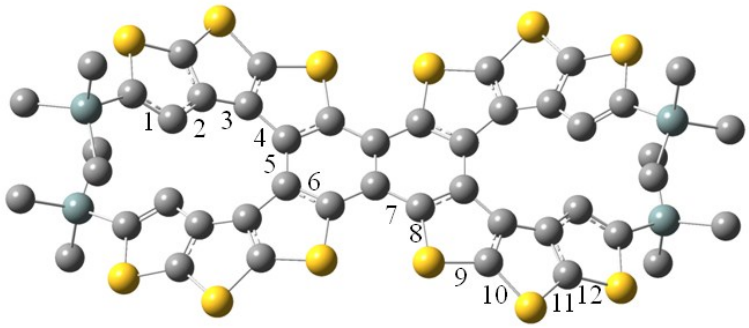
Table S1. The main concerned bond length for compound **b-1** between experiment and calculation



Bond	B3LYP	Experiment	Difference
1	1.374	1.382	-0.008
2	1.434	1.410	0.024
3	1.452	1.460	-0.008
4	1.447	1.457	-0.010
5	1.427	1.458	-0.031
6	1.407	1.408	-0.001
7	1.431	1.445	-0.014
8	1.778	1.766	0.012
9	1.735	1.716	0.019
10	1.750	1.752	-0.002
11	1.751	1.743	0.008
12	1.731	1.744	-0.013

Note: the difference is equal to calculation value minus experimental value.

Table S2. The calculated excitation energies, oscillator strengths and rotational strengths for compound **a-1** in the gas phase at the TD-B3LYP/ 6-31+G(d) level

states	eV	λ[a]	*f* [b]	R(length)[c]	R(velocity)[c]
1	3.0863	401.73	0.0047	-4.5446	-4.5063
2	3.1724	390.83	0.1079	49.7461	47.0734
3	3.4568	358.67	1.0445	-322.1801	-314.3870
4	3.5759	346.72	0.1039	63.2617	62.2392
5	3.6321	341.36	0.0000	0.0012	0.0012
6	3.6902	335.98	0.0019	-7.3021	-7.5226
7	3.7187	333.41	0.3889	-48.7064	-46.6584
8	3.8061	325.75	0.0001	1.8660	2.1389
9	3.8172	324.81	0.0007	-1.9063	-2.2540
10	3.8591	321.28	0.0024	22.7132	22.4641
11	3.8808	319.48	0.0094	6.8409	6.2753
12	3.8843	319.19	0.0492	119.7133	116.7099
13	3.9053	317.48	0.0007	0.3541	0.3258
14	3.9053	317.47	0.0152	7.2338	6.6363
15	3.9386	314.79	0.0053	24.0212	30.4695
16	3.9912	310.64	0.0000	-0.0005	-0.0005
17	4.0141	308.87	0.0035	-13.2801	-12.5949
18	4.0151	308.80	0.0000	0.0004	0.0004
19	4.0349	307.28	0.0281	-31.0832	-29.3246
20	4.0600	305.38	0.0104	-21.4989	-20.1204
21	4.0686	304.73	0.0000	0.0036	0.0035
22	4.0829	303.67	0.0000	0.0041	0.0038
23	4.1241	300.64	0.1580	4.3039	4.3471
24	4.1461	299.04	0.0017	-0.2112	-0.2390
25	4.1823	296.45	0.0042	29.2515	25.3589
26	4.2714	290.27	0.0206	-87.9517	-77.9490
27	4.2844	289.38	0.0725	-12.0661	-11.7603
28	4.3174	287.17	0.0000	-0.0055	-0.0057
29	4.3730	283.52	0.0000	0.0028	0.0054
30	4.3744	283.43	0.0128	8.5173	8.3874
31	4.3871	282.61	0.0150	25.5597	24.7837
32	4.4237	280.28	0.0000	-0.0023	-0.0022
33	4.4476	278.77	0.0057	2.9771	2.7757
34	4.4517	278.51	0.0109	1.0915	1.0903
35	4.4630	277.81	0.0000	0.0031	0.0038
36	4.4754	277.04	0.0349	-29.6402	-28.2410
37	4.4797	276.77	0.0220	3.2031	2.9920
38	4.5070	275.10	0.0008	-6.2383	-7.2354
39	4.5135	274.70	0.0186	5.3431	4.9553
40	4.5164	274.52	0.0089	-68.2526	-63.7132
41	4.5245	274.03	0.0157	-2.0731	-2.0363
42	4.5292	273.75	0.0000	0.2807	0.2814
43	4.5479	272.62	0.0343	166.7376	168.9089
44	4.5548	272.21	0.0183	35.2211	33.8545

45	4.5683	271.40	0.0000	-0.0411	-0.0857
46	4.5730	271.12	0.0246	-34.9630	-34.4344
47	4.5749	271.01	0.0012	18.8557	9.9096
48	4.5791	270.76	0.0384	64.9271	61.6046
49	4.5880	270.24	0.1125	-19.4526	-18.6733
50	4.5943	269.86	0.0011	-10.3381	-10.1221
51	4.6235	268.16	0.0028	-6.5605	-5.7661
52	4.6303	267.76	0.0166	10.5961	9.8594
53	4.6419	267.10	0.0000	0.0176	0.0083
54	4.6468	266.82	0.0860	45.5050	42.8182
55	4.6641	265.83	0.0001	2.6438	1.8085
56	4.6814	264.85	0.0205	-3.8350	-3.7928
57	4.6843	264.68	0.0000	0.0333	0.0307
58	4.6964	264.00	0.0004	-1.2473	-0.3353
59	4.7037	263.59	0.0331	-24.8137	-23.4488
60	4.7221	262.56	0.0000	0.2666	0.2562
61	4.7236	262.48	0.0001	0.9731	1.6789
62	4.7369	261.74	0.0105	38.0727	39.3940
63	4.7459	261.25	0.0188	-30.0529	-29.5524
64	4.7459	261.24	0.0002	12.6294	10.7195
65	4.7522	260.90	0.0210	-12.5870	-12.1597
66	4.7628	260.32	0.0052	-9.9692	-10.2952
67	4.7708	259.88	0.0069	11.0418	11.3024
68	4.7765	259.57	0.0011	13.7665	13.7623
69	4.7828	259.23	0.0000	0.0158	0.0153
70	4.7876	258.97	0.0001	0.0485	0.0488
71	4.8110	257.71	0.0693	334.0640	326.8443
72	4.8168	257.40	0.0004	1.6186	1.5561
73	4.8345	256.46	0.0014	0.8597	0.7911
74	4.8409	256.12	0.0001	0.5680	0.5572
75	4.8444	255.93	0.0618	-79.3180	-75.2677
76	4.8597	255.13	0.0522	20.8158	19.8597
77	4.8704	254.57	0.1487	-42.3446	-41.1880
78	4.8745	254.35	0.0226	-4.3350	-4.0199
79	4.8770	254.22	0.0000	1.2840	3.9233
80	4.8790	254.12	0.0000	0.2608	0.2953
81	4.9075	252.64	0.0597	39.9947	39.9140
82	4.9274	251.62	0.0002	-0.5432	-0.2972
83	4.9460	250.68	0.0023	9.5728	9.7417
84	4.9482	250.57	0.0123	58.4294	57.7177
85	4.9531	250.32	0.0002	-2.6118	-6.2603
86	4.9578	250.08	0.0000	-0.0031	-0.0067
87	4.9646	249.74	0.0319	-10.6980	-10.6344
88	4.9747	249.23	0.1753	-114.8786	-110.3011
89	4.9762	249.15	0.0067	56.8430	59.4860
90	4.9866	248.64	0.0002	1.1220	1.1084
91	4.9875	248.59	0.0073	-17.0624	-15.7708
92	4.9952	248.21	0.0005	0.5346	0.3795
93	4.9961	248.16	0.0001	0.4844	0.4645
94	5.0064	247.65	0.0567	-64.8294	-63.0271

95	5.0160	247.18	0.0129	41.7535	44.2869
96	5.0185	247.05	0.0765	-15.7408	-15.5485
97	5.0205	246.96	0.0555	-9.0779	-8.9051
98	5.0256	246.70	0.0105	37.2981	35.8299
99	5.0374	246.13	0.0000	0.0325	0.0367
100	5.0525	245.39	0.0000	0.1091	0.1049

[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.

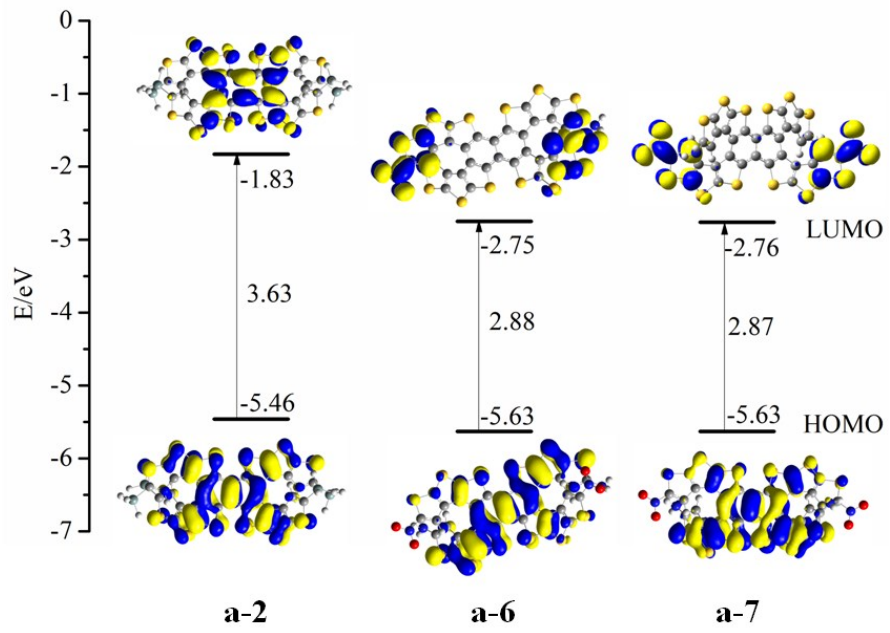


Fig. S1 HOMO and LUMO surfaces and energy gaps for **a-2**, **a-6** and **a-7**.

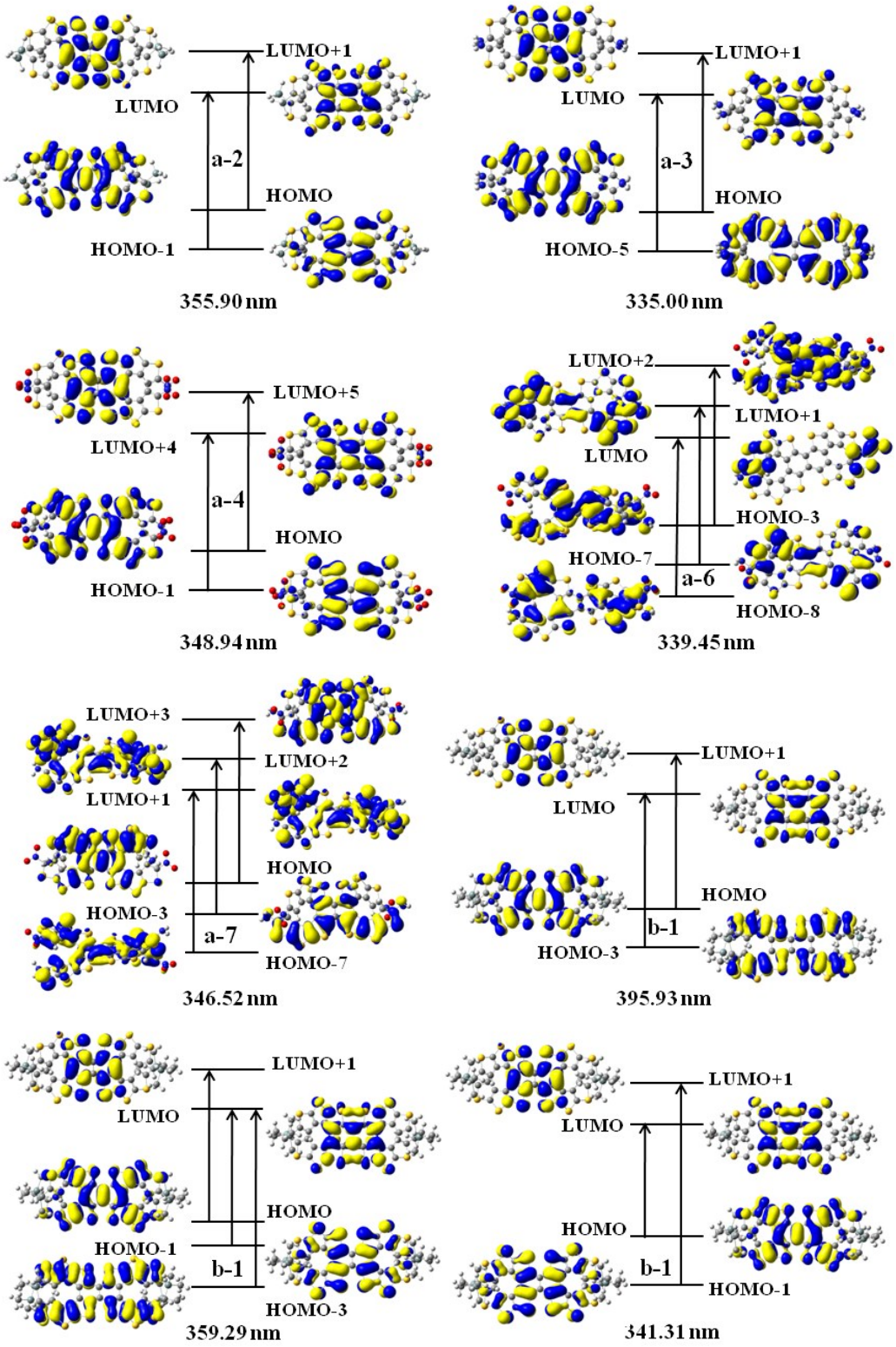


Fig. S2 Molecular orbital isosurfaces involved in the main electron transitions of compounds **a-(2 -4)**, **a-(6-7)** and **b-1** at the TDB3LYP/6-31+G(d) level of theory.

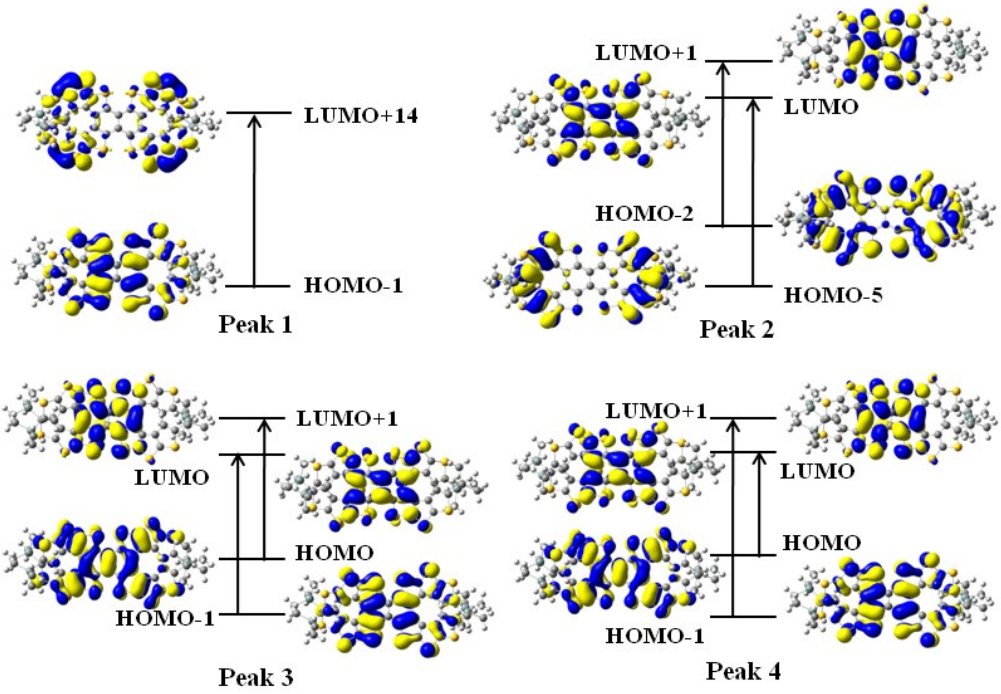
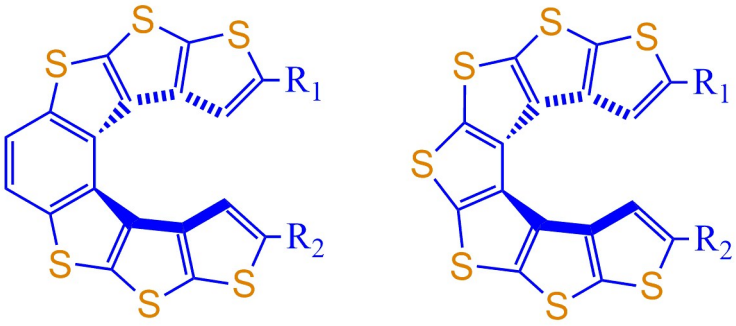


Fig. S3 Molecular orbitals involved into the main ECD transitions of compound **a-1**.



a' **c**

a'-1:R_1=R_2=$Si(CH_3)_3$
a'-3:R_1=R_2=NH_2
a'-4:R_1=R_2=NO_2
a'-7:R_1=NO_2**;** R_2=NH_2

c:R_1=R_2=$Si(CH_3)_3$

Fig. S4 Chemical structures of mono-helicene and its derivatives.