Electronic Supplementary Material (ESI) for RSC Advances.

Theoretical Study on the Electronic Structure and Second-Order Nonlinear Optical Properties of Benzannulated or Selenophene-annulated Expanded

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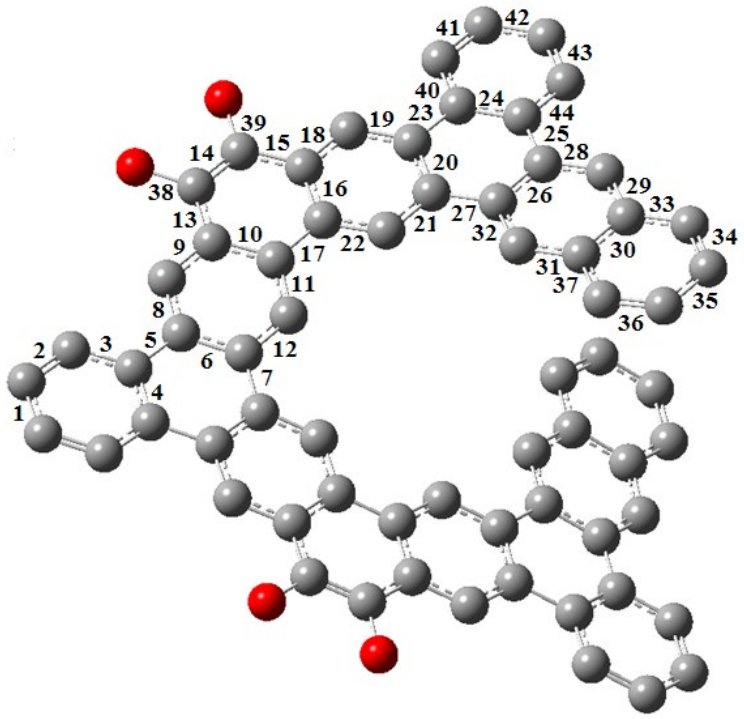
Table S1. The selected bond lengths for helicene **H1** between experiment and calculation.



Optimized geometry of helicene **H1** (not show hydrogens)

Bond	B3LYP	Experiment	Difference
1	1.399	1.405	0.006
2	1.384	1.390	-0.006
3	1.411	1.425	-0.014
4	1.420	1.417	0.003
5	1.469	1.487	-0.018
6	1.427	1.420	0.007
7	1.468	1.463	0.005
8	1.397	1.396	0.001
9	1.400	1.397	0.003
10	1.429	1.426	0.003
11	1.398	1.396	0.002
12	1.400	1.378	0.002
13	1.434	1.434	0.000
14	1.365	1.365	0.000
15	1.439	1.424	0.015
16	1.425	1.408	0.017
17	1.462	1.456	0.006

18	1.398	1.405	-0.007
19	1.396	1.385	0.011
20	1.427	1.431	-0.004
21	1.399	1.379	0.020
22	1.400	1.410	-0.010
23	1.471	1.476	-0.005
24	1.419	1.416	0.003
25	1.473	1.472	0.001
26	1.440	1.442	-0.002
27	1.473	1.471	0.002
28	1.390	1.389	0.001
29	1.408	1.422	0.014
30	1.431	1.416	0.015
31	1.408	1.402	0.006
32	1.391	1.378	0.013
33	1.423	1.419	0.004
34	1.374	1.363	0.011
35	1.420	1.404	0.016
36	1.374	1.374	0.000
37	1.423	1.430	-0.007
38	1.392	1.384	0.008
39	1.360	1.393	-0.033
40	1.410	1.419	-0.009
41	1.385	1.396	-0.011
42	1.399	1.404	-0.005
43	1.385	1.398	-0.013
44	1.410	1.414	-0.004

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

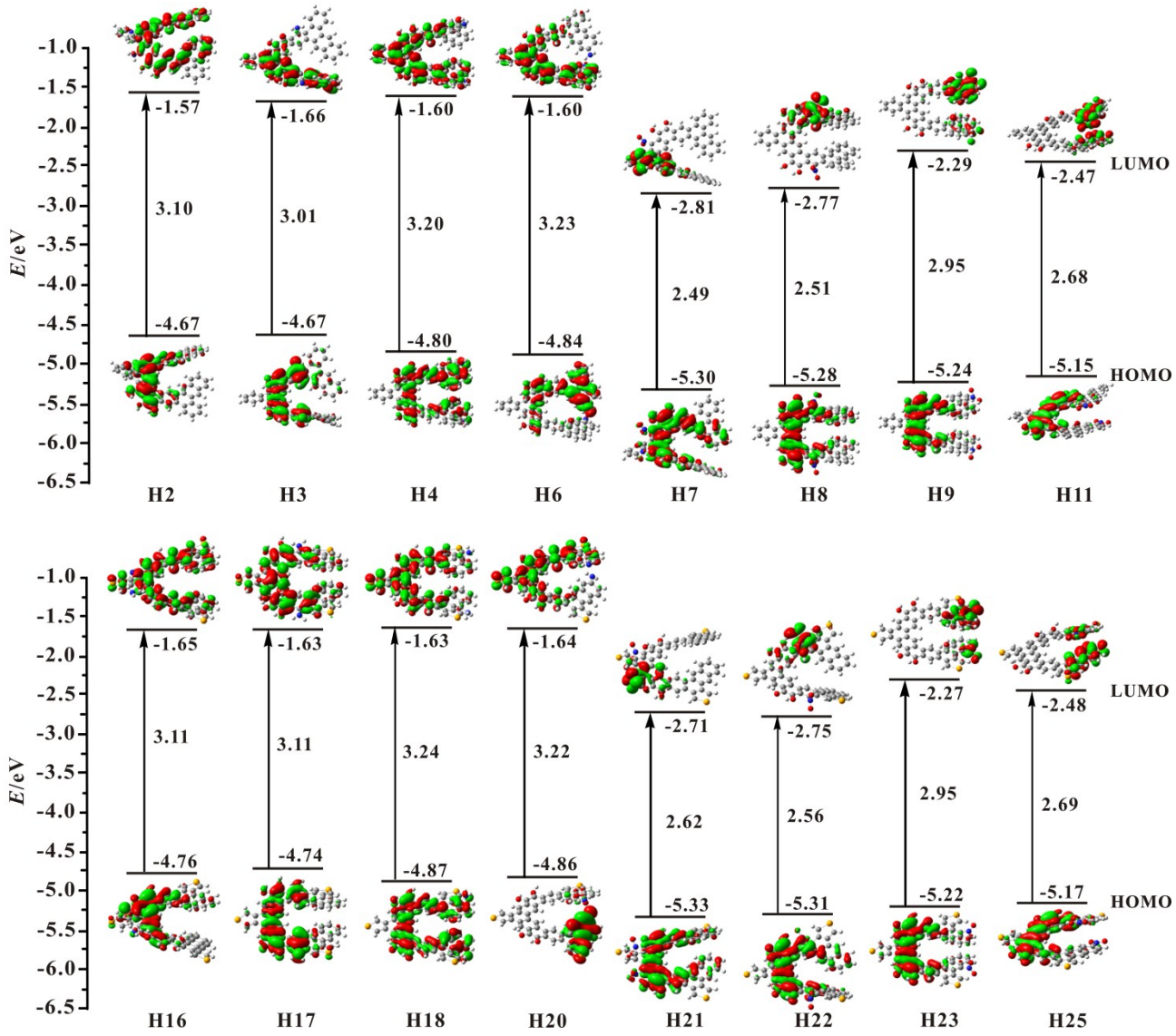


Fig. S1. Contour plots of the HOMO and LUMO for the studied helicenes **H2**-**H4**, **H6**-**H9**, **H11**, **H16**-**H18** and **H20**-**H23,** and **H25**.

Table S2. The computed main energy absorption band (λ, nm) using the B3LYP functional at the different basis sets level for helicene **H1**.

Basis set	6-31G(d)	6-31G(d,p)	6-31+G(d)	6-311+G(d)
λ	311.90	312.22	318.21	319.91

Table S3. The computed main energy absorption band (λ, nm) using the different functionals at 6-31+G(d) basis set level for helicene **H1**.

Functional	B3LYP	M06-2X	CAM-B3LYP	BH&HLYP
λ	318.21	301.10	300.13	298.83

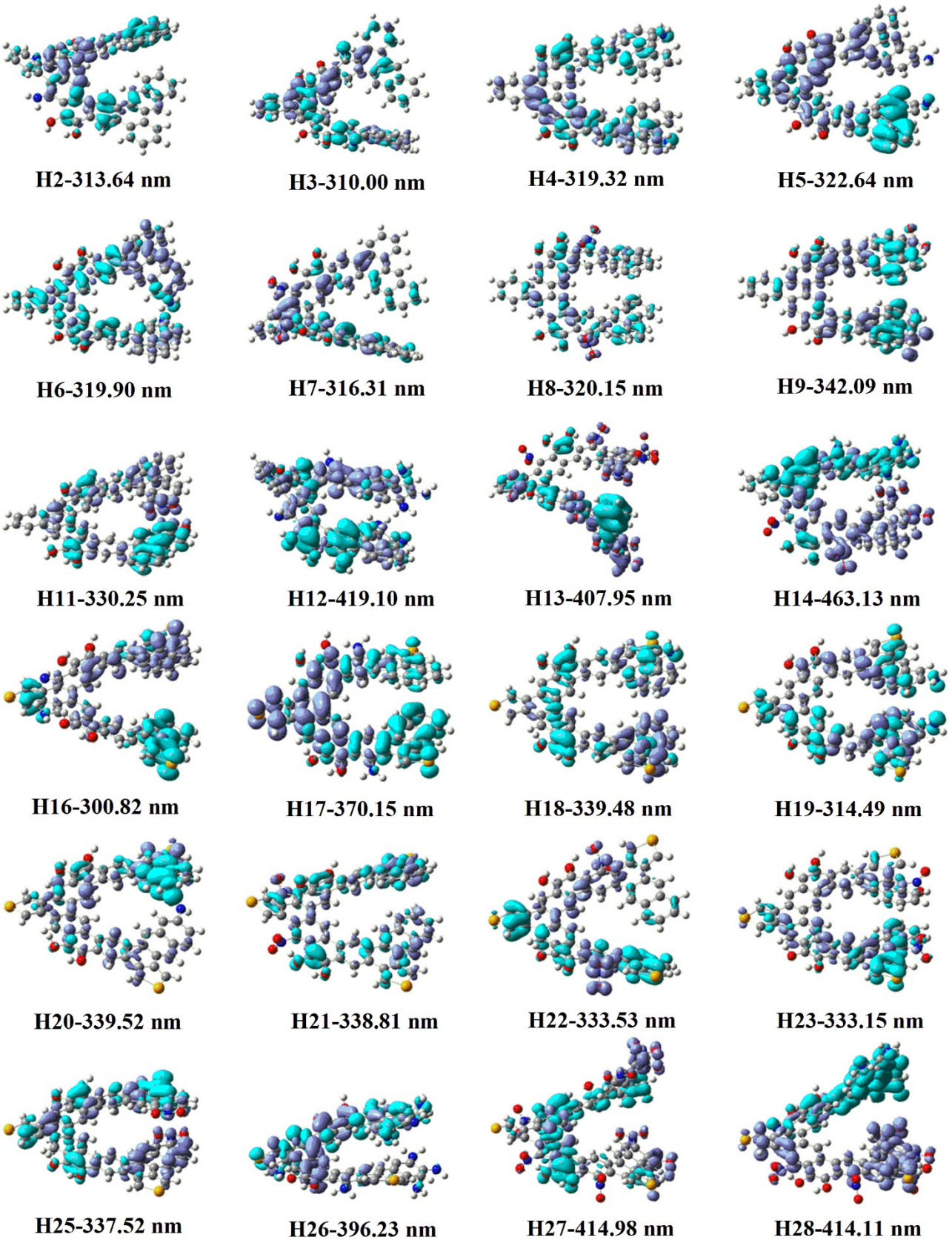


Fig. S2. Electron density difference maps of helicenes **H2**-**H9**, **H11**-**H14**, **H16**-**H23** and **H25**-**H28**. Blue and purple colours indicate depletion and accumulation of electron density, respectively.

Table S4. The calculated β_{HRS} values ($\times 10^{-30}$ esu) of helicenes **H1**-**H14** by using four DFT functionals associated with the 6-31+G(d) basis set and the calculated β_{HRS} values ($\times 10^{-30}$ esu) of the helicenes **H15**-**H28** by using four DFT functionals associated with the 6-31+G(d) for O, N, C and H atoms and LANL2DZ basis set for Se atom.

Compound	B3LYP	CAM-B3LYP	M06-2X	BH&HLYP
H1	7.67	5.26	5.52	4.97
H2	17.61	10.57	11.26	10.36
H3	7.87	4.86	5.18	4.80
H4	6.55	5.02	5.28	4.83
H5	14.99	9.41	10.07	9.93
H6	7.03	5.59	6.06	5.48
H7	15.93	8.39	7.77	9.12
H8	22.67	11.04	10.31	10.71
H9	16.08	9.70	10.19	9.64
H10	62.78	28.88	28.66	31.46
H11	24.64	14.11	14.34	14.47
H12	16.28	10.16	10.99	10.05
H13	46.40	22.23	23.74	24.03
H14	50.51	18.21	19.26	19.65
H15	8.79	5.89	6.10	5.58
H16	14.72	8.50	8.84	8.46
H17	8.93	5.79	6.23	5.74
H18	7.78	5.72	5.78	5.44
H19	16.14	10.11	10.72	10.82
H20	8.84	5.90	6.27	5.87
H21	15.30	7.89	8.13	8.28
H22	17.31	7.96	7.47	7.58
H23	12.43	7.82	8.30	7.54
H24	65.19	29.95	29.80	32.47
H25	25.35	15.10	15.52	15.17

H26	13.54	8.30	8.63	8.67
H27	52.45	26.10	27.31	27.62
H28	38.33	15.29	16.21	16.28