Theoretical study on functionalized acrylonitrile compounds with large second-order nonlinear optical response

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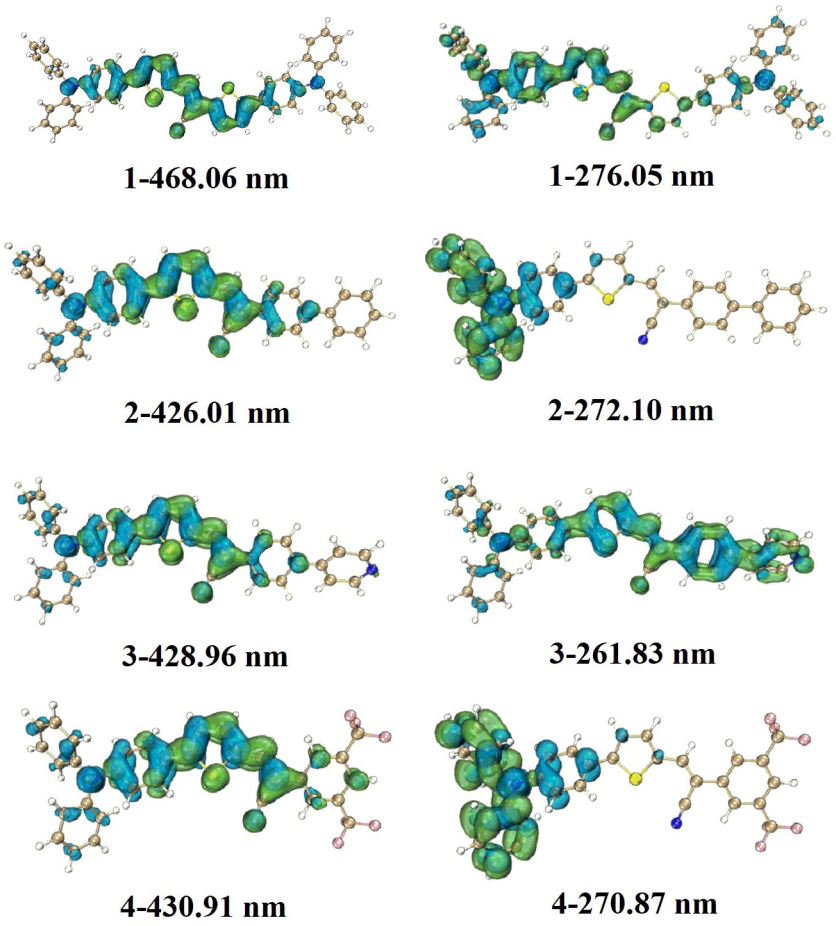


Fig.S1. Electron and hole distributions of two main absorption bands for compounds **1**-**4**, and the blue color and green color represent holes and electrons respectively.

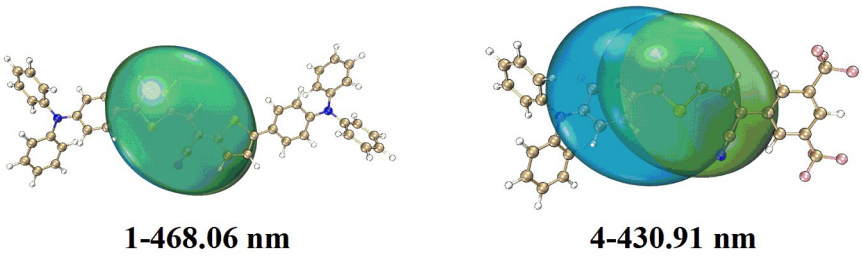
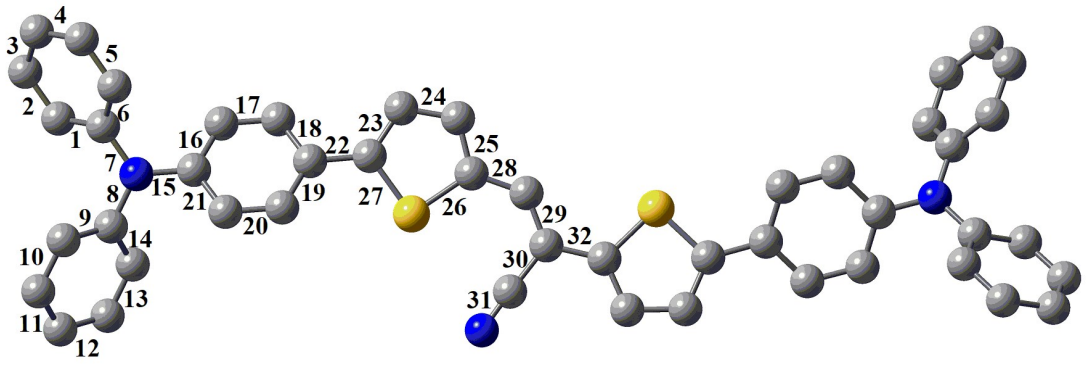


Fig.S2. Chole and Cele of the main absorption bands for compounds **1** and **4**, and the blue color and green color represent holes and electrons respectively.

Table S1. The selected bond lengths for compound **1** between experiment and calculation.



Optimized geometry of compound **1** (not show hydrogens)

Bond	D3-B3LYP		Experiment	Difference	
	gas	THF		gas	THF
1	1.402	1.402	1.397	0.005	0.005
2	1.393	1.393	1.382	0.011	0.011
3	1.396	1.397	1.376	0.020	0.021
4	1.396	1.397	1.387	0.009	0.010
5	1.392	1.393	1.373	0.019	0.020
6	1.402	1.402	1.398	0.004	0.004
7	1.420	1.422	1.403	0.017	0.019
8	1.420	1.421	1.431	-0.011	-0.010
9	1.402	1.402	1.392	0.010	0.010
10	1.393	1.393	1.393	0.000	0.000
11	1.396	1.397	1.378	0.018	0.019
12	1.396	1.397	1.380	0.016	0.017
13	1.393	1.393	1.393	0.000	0.000
14	1.401	1.402	1.379	0.022	0.023
15	1.408	1.405	1.427	-0.019	-0.022
16	1.406	1.407	1.395	0.011	0.012
17	1.385	1.385	1.374	0.011	0.011
18	1.408	1.409	1.386	0.022	0.023
19	1.408	1.408	1.395	0.013	0.013
20	1.387	1.386	1.383	0.004	0.003
21	1.405	1.407	1.379	0.026	0.028
22	1.457	1.456	1.458	-0.001	-0.002
23	1.385	1.386	1.372	0.013	0.014

24	1.407	1.407	1.404	0.003	0.003
25	1.390	1.391	1.364	0.026	0.027
26	1.758	1.762	1.737	0.021	0.025
27	1.750	1.753	1.727	0.023	0.026
28	1.426	1.425	1.436	-0.010	-0.011
29	1.370	1.372	1.341	0.029	0.031
30	1.430	1.429	1.450	-0.020	-0.021
31	1.165	1.165	1.148	0.017	0.017
32	1.454	1.455	1.464	-0.010	-0.009

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

Table S2. The computed absorption wavelengths (λ, nm) using the B3LYP functional at the different basis sets level for compound **1** along with the experimental values.

Basis set	6-31G(d)	6-31G(d,p)	6-31+G(d)	6-31+G(d,p)	6-31++G(d,p)	Exp
Band1	331.61	332.10	341.82	342.90	342.49	304
Band2	552.28	552.82	562.20	562.90	562.83	482

Table S3. The computed absorption wavelengths (λ, nm) using the B3LYP functional at the different basis sets level for compound **4** along with the experimental values.

Basis set	6-31G(d)	6-31G(d,p)	6-31+G(d)	6-31+G(d,p)	6-31++G(d,p)	Exp
Band1	377.14	377.56	384.07	384.61	384.63	286
Band2	522.27	522.82	535.21	535.95	535.92	439

Table S4. The computed absorption wavelength (λ, nm) in gas and solution (in parentheses) phases, using the different functionals at 6-31G(d) basis set level for compound **1** along with the experimental values.

Functional	B3LYP	B3LYP-D3	CAM-B3LYP(in THF)	BH&HLYP	Exp
Band1	331.61	338.88	272.96(276.05)	272.64	304
Band2	552.28	590.27	447.93(468.06)	452.04	482

Table S5. The calculated β_{HRS} values ($\times 10^{-30}$ esu) of the compound **1** by using three

DFT functionals associated with the 6-31+G(d) basis set and using CAM-B3LYP/6-31G(d) basis set (in parentheses).

Functional	B3LYP	CAM-B3LYP	M06-2X
β_{HRS}	24.72	19.55(18.57)	21.00

Table S6. Cartesian Coordinates for compound **1**, optimized at the B3LYP-D3/6-31G(d) level of theory

Center Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	S	-2.966332	-0.175034	0.010299
2	S	2.982549	-0.526259	-0.001529
3	N	1.137296	-3.31304	-0.049193
4	N	-9.74081	0.353822	0.031173
5	N	9.727825	0.199748	0.01005
6	C	-4.291556	-1.329229	-0.036175
7	C	-3.796875	-2.615677	-0.076215
8	H	-4.437096	-3.488348	-0.132954
9	C	-2.382677	-2.687719	-0.079894
10	H	-1.822575	-3.614835	-0.11992
11	C	-1.766271	-1.452966	-0.044899
12	C	-0.338042	-1.178811	-0.046886
13	C	0.20276	0.080398	-0.050891
14	H	-0.504493	0.907584	-0.060741
15	C	1.562753	0.511139	-0.046349
16	C	1.953348	1.845237	-0.073232
17	H	1.231127	2.654325	-0.107019
18	C	3.347615	2.034839	-0.070354
19	H	3.820355	3.008566	-0.120915
20	C	4.06409	0.850011	-0.039132
21	C	5.509658	0.670563	-0.028164
22	C	6.359742	1.720684	0.369353
23	H	5.930186	2.658225	0.707892
24	C	7.737161	1.569643	0.3852
25	H	8.368387	2.38808	0.713029
26	C	8.328347	0.354529	-0.003589
27	C	7.490051	-0.700302	-0.402637
28	H	7.928734	-1.640374	-0.71783
29	C	6.112475	-0.543106	-0.409134
30	H	5.492931	-1.368214	-0.74868
31	C	0.494961	-2.341609	-0.047039
32	C	-5.679504	-0.88408	-0.018658
33	C	-6.053818	0.408477	-0.428603
34	H	-5.296561	1.095324	-0.796074
35	C	-7.379848	0.81632	-0.418129
36	H	-7.643615	1.812613	-0.755451

37	C	-8.391608	-0.055976	0.014716
38	C	-8.029019	-1.347495	0.43358
39	H	-8.796482	-2.027381	0.787064
40	C	-6.70237	-1.749636	0.413991
41	H	-6.446255	-2.740805	0.774869
42	C	10.571813	1.293019	-0.319572
43	C	10.269366	2.118367	-1.411649
44	H	9.384724	1.912272	-2.005004
45	C	11.098737	3.191871	-1.726844
46	H	10.852877	3.823843	-2.575661
47	C	12.247063	3.445272	-0.974077
48	H	12.895603	4.278535	-1.227268
49	C	12.554495	2.615996	0.106345
50	H	13.442289	2.805035	0.703302
51	C	11.720962	1.551343	0.440413
52	H	11.952689	0.911997	1.285744
53	C	10.310665	-1.050664	0.34729
54	C	11.402023	-1.538785	-0.384459
55	H	11.78885	-0.956077	-1.213762
56	C	11.981521	-2.758559	-0.043922
57	H	12.826951	-3.125708	-0.618991
58	C	11.472737	-3.51436	1.013973
59	H	11.921844	-4.46882	1.271435
60	C	10.381112	-3.031235	1.738174
61	H	9.980113	-3.605728	2.568405
62	C	9.807416	-1.803331	1.417604
63	H	8.96749	-1.421018	1.987905
64	C	-10.079066	1.689795	0.369332
65	C	-9.434004	2.338434	1.43217
66	H	-8.674578	1.808185	1.997212
67	C	-9.766794	3.65159	1.75518
68	H	-9.258285	4.141607	2.580821
69	C	-10.756952	4.329004	1.040922
70	H	-11.019155	5.350161	1.30071
71	C	-11.407032	3.679402	-0.010111
72	H	-12.175331	4.196244	-0.578411
73	C	-11.067485	2.373031	-0.353149
74	H	-11.5645	1.872717	-1.177521
75	C	-10.770087	-0.566181	-0.298237
76	C	-10.613876	-1.450172	-1.375303
77	H	-9.698865	-1.421826	-1.957483
78	C	-11.625144	-2.354746	-1.689406
79	H	-11.490521	-3.034209	-2.52639
80	C	-12.810106	-2.3783	-0.951276
81	H	-13.599586	-3.07965	-1.203929
82	C	-12.970036	-1.49041	0.114347
83	H	-13.884415	-1.502211	0.700972
84	C	-11.956514	-0.595502	0.448138
85	H	-12.075596	0.086204	1.28366

Table S7. Cartesian Coordinates for compound **2**, optimized at the B3LYP-D3/6-31G(d) level of theory

Center Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	S	0.440981	-0.089514	0.044398
2	N	2.658109	2.308131	-0.565038
3	N	-6.336909	0.178418	-0.008194
4	C	3.825507	0.051473	-0.042284
5	C	3.103727	-1.090676	0.167178
6	H	3.679176	-2.001282	0.314442
7	C	1.69253	-1.313334	0.208725
8	C	1.111222	-2.561704	0.394015
9	H	1.706775	-3.460855	0.513941
10	C	-0.296067	-2.545369	0.393548
11	H	-0.90644	-3.435057	0.493172
12	C	-0.830139	-1.280651	0.209864
13	C	-2.234046	-0.894821	0.152016
14	C	-3.231042	-1.732676	0.687697
15	H	-2.945894	-2.65508	1.183666
16	C	-4.571387	-1.384274	0.639235
17	H	-5.317503	-2.038969	1.075429
18	C	-4.975936	-0.176021	0.044108
19	C	-3.989332	0.668488	-0.493325
20	H	-4.282972	1.598621	-0.966709
21	C	-2.650001	0.315086	-0.434911
22	H	-1.914403	0.976396	-0.883762
23	C	3.164015	1.286309	-0.324816
24	C	-7.332273	-0.822597	-0.164634
25	C	-7.1608	-1.853506	-1.098951
26	H	-6.260352	-1.878607	-1.703788
27	C	-8.139177	-2.834091	-1.244084
28	H	-7.994297	-3.628034	-1.971375
29	C	-9.305899	-2.789756	-0.478349
30	H	-10.070169	-3.551465	-0.599819
31	C	-9.481607	-1.756253	0.443815
32	H	-10.38261	-1.713292	1.049272
33	C	-8.500169	-0.781867	0.609131
34	H	-8.629877	0.016608	1.332114
35	C	-6.732987	1.538297	0.098038
36	C	-7.738362	2.044604	-0.737051
37	H	-8.200352	1.390374	-1.468853
38	C	-8.138065	3.373743	-0.621686
39	H	-8.918418	3.754105	-1.274828
40	C	-7.531974	4.217699	0.31081
41	H	-7.840451	5.255551	0.392545
42	C	-6.525513	3.714836	1.137707

43	H	-6.050984	4.358936	1.872598
44	C	-6.13257	2.382055	1.042877
45	H	-5.359873	1.987091	1.693936
46	C	5.303158	0.089895	-0.021107
47	C	6.000534	1.110808	-0.688945
48	C	6.057351	-0.880988	0.660568
49	C	7.38937	1.141293	-0.698461
50	H	5.444902	1.877854	-1.219311
51	C	7.445127	-0.848175	0.646613
52	H	5.555757	-1.648116	1.241933
53	C	8.144716	0.160873	-0.036519
54	H	7.898236	1.923329	-1.253529
55	H	7.999196	-1.592358	1.210605
56	C	9.623837	0.193446	-0.045943
57	C	10.369507	-0.99583	-0.091986
58	C	10.319254	1.413113	-0.009466
59	C	11.762175	-0.967115	-0.100815
60	H	9.850316	-1.948009	-0.149275
61	C	11.711903	1.44237	-0.019899
62	H	9.76182	2.342801	0.055317
63	C	12.440008	0.252428	-0.065174
64	H	12.319079	-1.898982	-0.145239
65	H	12.229734	2.396779	0.017152
66	H	13.525958	0.275367	-0.072616

Table S8. Cartesian Coordinates for compound **3**, optimized at the B3LYP-D3/6-31G(d) level of theory

Center	Atomic	Coordinates (Angstroms)		
Number	Type	X	Y	Z
1	S	0.442168	-0.084708	0.073066
2	N	2.663498	2.339057	-0.363996
3	N	-6.334014	0.172797	-0.034422
4	C	3.828544	0.054042	0.021329
5	C	3.103586	-1.077897	0.274346
6	H	3.675478	-1.978486	0.483144
7	C	1.692957	-1.293247	0.332771
8	C	1.110284	-2.525119	0.607209
9	H	1.705212	-3.413265	0.793833
10	C	-0.296242	-2.509528	0.597495
11	H	-0.90778	-3.389166	0.759289
12	C	-0.829113	-1.261714	0.316284
13	C	-2.232486	-0.882378	0.223849
14	C	-3.230419	-1.673905	0.824658
15	H	-2.945919	-2.551639	1.396288
16	C	-4.570642	-1.33163	0.744524
17	H	-5.317421	-1.94858	1.231566
18	C	-4.974239	-0.17647	0.050735

19	C	-3.986295	0.621502	-0.552256
20	H	-4.279458	1.508658	-1.10203
21	C	-2.647207	0.27499	-0.461726
22	H	-1.91062	0.897202	-0.961929
23	C	3.168896	1.30331	-0.192096
24	C	-7.332468	-0.834849	-0.106506
25	C	-7.156755	-1.950619	-0.936778
26	H	-6.24985	-2.037708	-1.525929
27	C	-8.139658	-2.935337	-1.000526
28	H	-7.991282	-3.795137	-1.647809
29	C	-9.315191	-2.812343	-0.257183
30	H	-10.083009	-3.577882	-0.315439
31	C	-9.495037	-1.694859	0.56029
32	H	-10.402936	-1.58961	1.147523
33	C	-8.509275	-0.714593	0.645143
34	H	-8.642633	0.149218	1.287819
35	C	-6.726812	1.538379	-0.052916
36	C	-7.714549	1.973591	-0.946651
37	H	-8.165999	1.260164	-1.628018
38	C	-8.110816	3.308797	-0.952888
39	H	-8.877618	3.63382	-1.650417
40	C	-7.518233	4.227847	-0.08493
41	H	-7.823977	5.26962	-0.097909
42	C	-6.529043	3.795171	0.800427
43	H	-6.065338	4.498516	1.486251
44	C	-6.14012	2.458028	0.827147
45	H	-5.381288	2.118449	1.524345
46	C	5.305961	0.076984	-0.026015
47	C	6.057511	-1.089248	-0.254354
48	C	6.005926	1.282533	0.154307
49	C	7.444878	-1.05382	-0.273083
50	H	5.555519	-2.033019	-0.440911
51	C	7.39442	1.314468	0.134832
52	H	5.452348	2.20309	0.309362
53	C	8.144539	0.147545	-0.074812
54	H	7.997183	-1.974938	-0.432036
55	H	7.904888	2.264536	0.258787
56	C	9.621762	0.182318	-0.098114
57	C	10.34989	1.054634	0.724173
58	C	10.365907	-0.654757	-0.942455
59	C	11.741273	1.048368	0.664695
60	H	9.840143	1.7123	1.42114
61	C	11.756552	-0.582859	-0.923748
62	H	9.868017	-1.334982	-1.626241
63	N	12.453905	0.249093	-0.139596
64	H	12.315455	1.717866	1.302852
65	H	12.342765	-1.224358	-1.579549

Table S9. Cartesian Coordinates for compound **4**, optimized at the B3LYP-D3/6-31G(d) level of theory

Center Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	S	0.14181	-0.084226	0.044162
2	N	2.359879	2.336608	-0.48496
3	N	-6.631146	0.148403	-0.030282
4	C	3.524243	0.068276	-0.017354
5	C	2.80565	-1.058384	0.277557
6	H	3.381333	-1.948366	0.519432
7	C	1.398334	-1.276861	0.346749
8	C	0.82204	-2.500482	0.67209
9	H	1.42167	-3.378009	0.891097
10	C	-0.58308	-2.4909	0.667512
11	H	-1.190911	-3.365391	0.866117
12	C	-1.122324	-1.256076	0.338562
13	C	-2.526803	-0.886843	0.238294
14	C	-3.517695	-1.654605	0.880706
15	H	-3.226232	-2.505758	1.487939
16	C	-4.859147	-1.319491	0.797218
17	H	-5.599554	-1.91626	1.317736
18	C	-5.272086	-0.195899	0.057343
19	C	-4.290524	0.576949	-0.589061
20	H	-4.590258	1.438003	-1.175327
21	C	-2.950311	0.23824	-0.494392
22	H	-2.21976	0.839475	-1.02805
23	C	2.864466	1.307342	-0.275634
24	C	-7.634407	-0.857764	-0.026338
25	C	-7.47497	-2.023556	-0.788202
26	H	-6.576424	-2.152047	-1.382544
27	C	-8.46401	-3.004152	-0.778712
28	H	-8.328663	-3.903141	-1.373422
29	C	-9.62947	-2.82782	-0.030288
30	H	-10.402141	-3.590643	-0.031902
31	C	-9.79328	-1.660597	0.718143
32	H	-10.693415	-1.513264	1.30818
33	C	-8.801154	-0.683196	0.730033
34	H	-8.922172	0.219942	1.318794
35	C	-7.023483	1.51197	-0.12601
36	C	-8.010302	1.895838	-1.043406
37	H	-8.461408	1.145006	-1.68356
38	C	-8.406003	3.228807	-1.124952
39	H	-9.172181	3.514715	-1.839993
40	C	-7.813617	4.194592	-0.309097
41	H	-8.119051	5.234056	-0.380656
42	C	-6.825626	3.812312	0.600389
43	H	-6.362727	4.552916	1.246297

44	C	-6.437375	2.478547	0.702251
45	H	-5.679716	2.177954	1.418441
46	C	5.002588	0.091892	-0.058611
47	C	5.696447	1.305503	0.073004
48	C	5.751072	-1.081446	-0.240738
49	C	7.088364	1.334967	0.049648
50	H	5.144993	2.231735	0.188959
51	C	7.142268	-1.043072	-0.25757
52	H	5.254834	-2.029892	-0.407067
53	C	7.8257	0.163185	-0.110404
54	H	8.907711	0.192569	-0.144508
55	C	7.914512	-2.327323	-0.398051
56	C	7.807626	2.641083	0.261489
57	F	7.237806	-3.24182	-1.127954
58	F	8.158201	-2.889235	0.808136
59	F	9.109694	-2.132375	-0.992683
60	F	7.086929	3.68972	-0.185329
61	F	9.000135	2.661254	-0.372357
62	F	8.053692	2.857203	1.573647