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Supporting Information

Nonlinear Properties of Intramolecular Charge-Transfer Compounds Based on Benzothiadiazole

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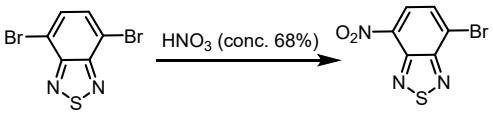
1. Experimental section

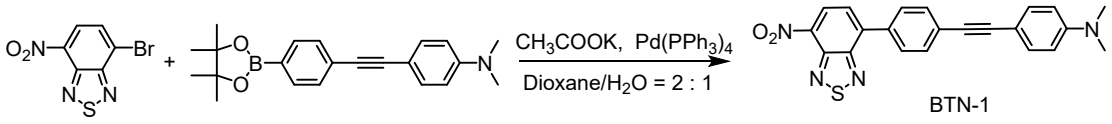
1.1 Materials and reagents.

All commercial chemical reagents were purchased from Admas and used directly without purification. Column chromatography mainly used silica gel with 100-200 mesh and 200-300 mesh specifications for purification and separation, respectively. Dry solvents are all purchased from Tansoole Platform (Shanghai Titan Technology Co. Ltd.) and Energy Chemical. All air and moisture-sensitive reactions were carried out in an argon atmosphere. *N,N*-dimethyl-4-((4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)ethynyl)aniline, (*E*)-(2-(4-(4-(dimethylamino)styryl)phenyl)-4,5,5-trimethyl-1,3,2-dioxaborolan-4-yl)methylium, (*E*)-4-(4-ethynylstyryl)-*N,N*-dimethylaniline and 4-bromo-7-nitrobenzo[c][1,2,5]thiadiazole were prepared according to the literature methods.[1, 2]

1.2 Syntheses and Characterizations



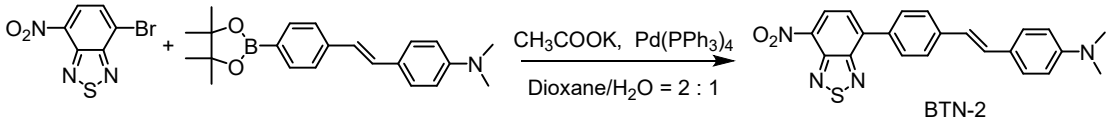
***N,N*-dimethyl-4-((4-(7-nitrobenzo[c][1,2,5]thiadiazol-4-yl)phenyl)ethynyl)aniline(BTN-1)**



A 50 mL three-neck round-bottom flask with a magnetic stir bar was added with *N*,*N*-dimethyl-4-((4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)ethynyl)aniline (330 mg, 0.95 mmol), 4-bromo-7-nitrobenzo[c][1,2,5]thiadiazole (273.6 mg, 1.05 mmol) and $Pd(PPh_3)_4$ (55.6 mg, 0.048 mmol). Then Potassium acetate (306mg, 3.12mmol) in dioxane (5 mL) and distilled water (2.5 mL) were added. The mixture was stirred at 90°C overnight under N_2 atmosphere. The reaction mixture was cooled down to room temperature and was quenched by adding H_2O. The reaction mixture was then washed with CH_2Cl_2 and dried with anhydrous Na_2SO_4. The filtrate was dried under reduced pressure and subjected to silica gel flash chromatography.

BTN-1. Chromatography (Petroleum ether/CH_2Cl_2, 2:1 v/v). Yield 53%, purple-black solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.77 (d, *J* = 8.0 Hz, 1H), 8.11 (dd, *J* = 9.9, 8.2 Hz, 3H), 7.71 (d, *J* = 8.4 Hz, 2H), 7.41 (d, *J* = 8.9 Hz, 2H), 6.74 (d, *J* = 9.0 Hz, 2H), 2.97 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 154.5, 150.4, 147.3, 141.12, 138.5, 134.4, 133, 131.7, 129.7, 128.1, 126.5, 125.7, 111.9, 109.5, 93.7, 87.5, 40.3. HRMS (ESI, *m/z*): calcd. for $C_{22}H_{16}N_4O_2S$ $[M+H]^+$: 401.1067; found: 401.1065.

(*E*)-*N,N*-dimethyl-4-(4-(7-nitrobenzo[c][1,2,5]thiadiazol-4-yl)styryl)aniline(BTN-2)

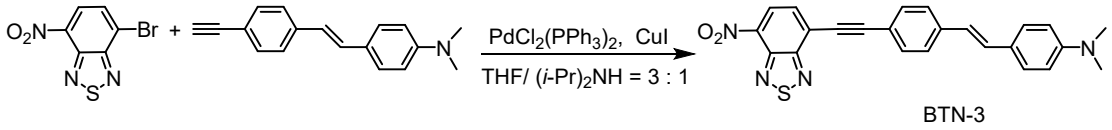


A 50 mL three-neck round-bottom flask with a magnetic stir bar was added with (*E*)-(2-(4-(4-(dimethylamino)styryl)phenyl)-4,5,5-trimethyl-1,3,2-dioxaborolan-4-yl)methylium (365 mg, 1.05 mmol), 4-bromo-7-nitrobenzo[c][1,2,5]thiadiazole (309.6 mg, 1.18 mmol) and $Pd(PPh_3)_4$ (64.7 mg, 0.056mmol). Then Potassium acetate (302 mg, 3.08 mmol) in dioxane (5 mL) and distilled water (2.5 mL) were added. The mixture was stirred at 85°C overnight under N_2 atmosphere. The reaction mixture was cooled down to room temperature and was quenched by adding H_2O. The reaction mixture was then washed with CH_2Cl_2 and dried with anhydrous Na_2SO_4.

The filtrate was dried under reduced pressure and subjected to silica gel flash chromatography.

BTN-2. Chromatography (Petroleum ether/CH_2Cl_2, 1:1 v/v). Yield 55%, purple solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.69 (d, J = 7.9 Hz, 1H), 7.99 (d, J = 8.4 Hz, 2H), 7.87 (d, J = 8.0 Hz, 1H), 7.67 (d, J = 8.4 Hz, 2H), 7.46 (d, J = 8.8 Hz, 2H), 7.20 (d, J = 16.3 Hz, 1H), 6.99 (d, J = 16.2 Hz, 1H), 6.73 (d, J = 8.8 Hz, 2H), 3.01 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 154.6, 150.6, 147.6, 141.8, 140.4, 138.2, 133.7, 131.0, 130.2, 128.3, 128.1, 127.7, 126.5, 125.2, 123.1, 112.4, 40.5. HRMS (ESI, m/z): calcd. for $C_{22}H_{18}N_4O_2S$ $[M+H]^+$: 403.1215, found: 403.1223.

(*E*)-*N,N*-dimethyl-4-(4-((7-nitrobenzo[c][1,2,5]thiadiazol-4-yl)ethynyl)styryl)aniline(BTN-3)



BTN-3

A 50 mL three-neck round-bottom flask with a magnetic stir bar was added with (*E*)-4-(4-ethynylstyryl)-*N,N*-dimethylaniline (251.2 mg, 1.02 mmol), and 4-bromo-7-nitrobenzo[c][1,2,5]thiadiazole (301.2mg, 1.16mmol), $PdCl_2(PPh_3)_2$ (38 mg, 0.033mmol) and CuI (32 mg, 0.168mmol). Then THF/ (i-Pr)$_2$NH (30 mL / 10 mL) was added. The mixture was stirred at room temperature for 6 h under Ar atmosphere. The mixture was dried under reduced pressure and subjected to silica gel flash chromatography.

BTN-3. Chromatography (Petroleum ether/CH_2Cl_2, 2:1 v/v). Yield 51%, purple-black solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.61 (d, J = 7.9 Hz, 1H), 7.89 (d, J = 7.9 Hz, 1H), 7.66 (d, J = 8.3 Hz, 2H), 7.53 (d, J = 8.2 Hz, 2H), 7.44 (d, J = 8.7 Hz, 2H), 7.15 (d, J = 16.2 Hz, 1H), 6.92 (d, J = 16.2 Hz, 1H), 6.72 (d, J = 8.9 Hz, 2H), 3.01 (s, 6H). 7.44 (d, J = 8.7 Hz, 2H), 7.15 (d, J = 16.2 Hz, 1H), 6.92 (d, J = 16.2 Hz, 1H), 6.72 (d, J = 8.9 Hz, 2H), 3.01 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.7, 153.9, 150.7, 142, 140.4, 137.5, 133.7, 131.0, 130.2, 129.9, 128.1, 127.7, 126.5, 125.2, 123.1, 112.4, 93.3, 40.5. HRMS (ESI, m/z): calcd. for $C_{24}H_{18}N_4O_2S$ $[M+H]^+$: 427.1223; found: 427.1217.

References

1. J. Kulhánek, F. Bureš and M. J. B. j. o. o. c. *Ludwig*, 2009, 5, 11.
2. C.-F. Yang, L.-Y. Zeng, B.-K. Ning, J.-Y. Wang, H. Zhang, Z.-H. J. S. A. P. A. M. Zhang and B. *Spectroscopy*, 2020, 225, 117482.

2. Optical Properties

2.1 UV-vis absorption measurements

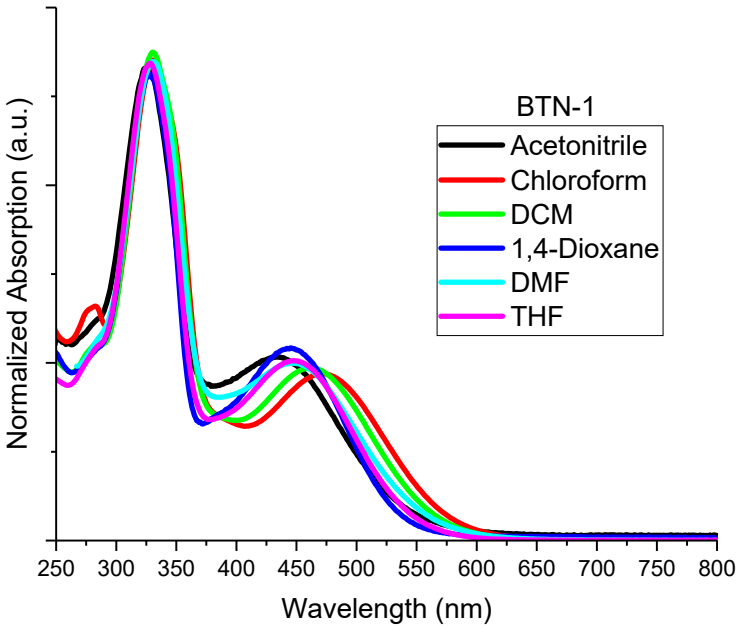


Fig. S1 Optical absorption spectra of the chromophores BTN-1 in solvents of varying polarity

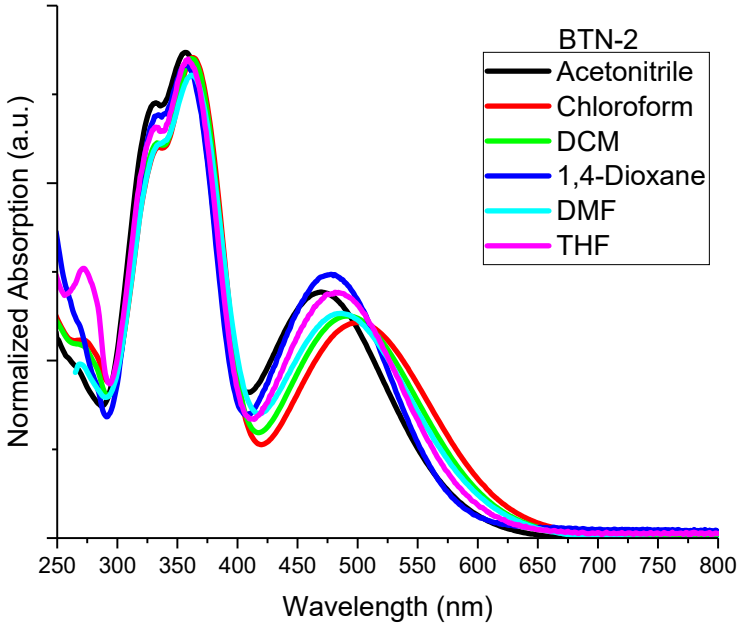


Fig. S2 Optical absorption spectra of the chromophores BTN-2 in solvents of varying polarity

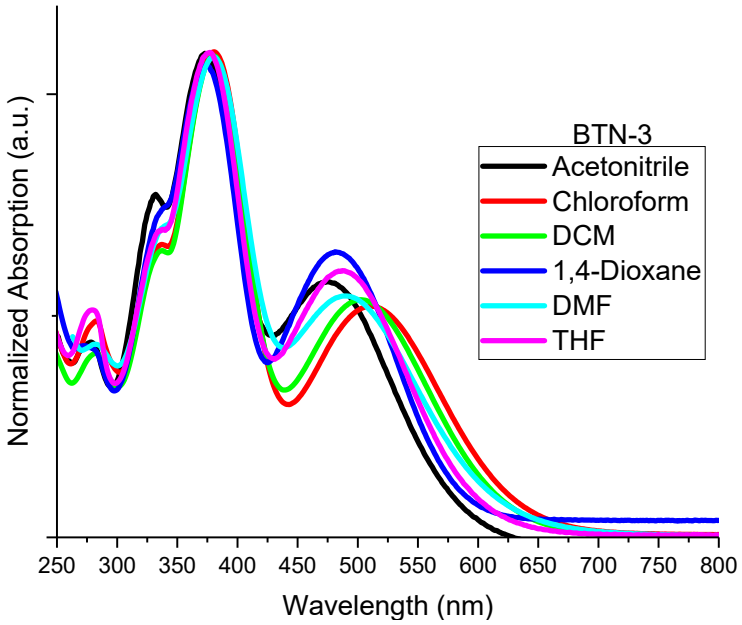


Fig. S3 Optical absorption spectra of the chromophores BTN-3 in solvents of varying polarity.

The particular behavior observed from BTN-1, BTN-2 and BTN-3 is the change in spectral shape in different solvents (Fig. S1-3), which shows some subtle effects. From Fig. S1-3, the largest red-shift is chloroform followed by dichlorine, and the largest blue shift is 1,4-Dioxane followed by THF and DMF. This is one of the reasons why chloroform was chosen as the solventization model in the theoretical calculations.

2.2 Fluorescence emission spectra

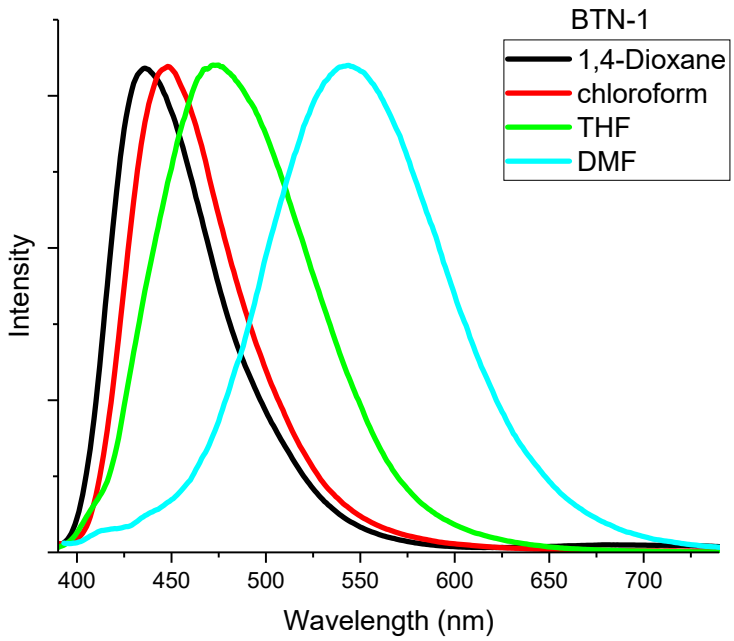


Fig. S4 Fluorescence emission spectra of the chromophores BTN-1 in solvents of varying polarity.

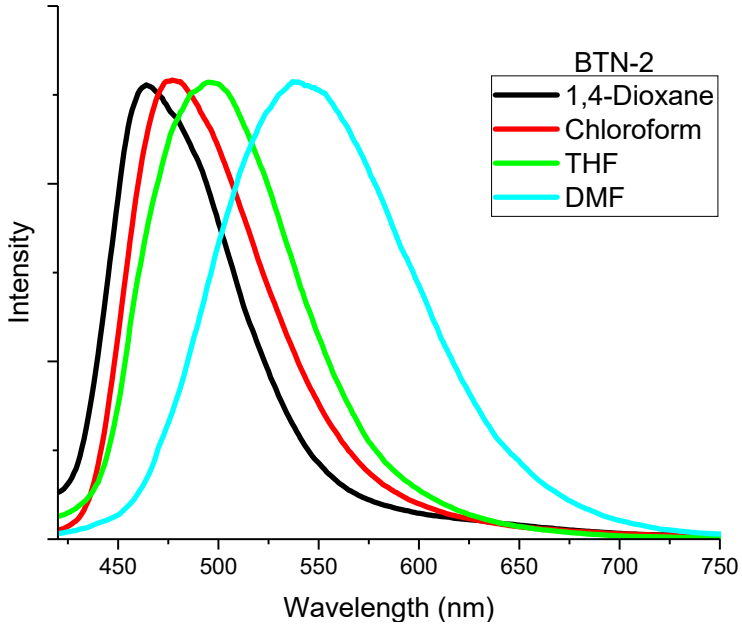


Fig. S5 Fluorescence emission spectra of the chromophores BTN-2 in solvents of varying polarity.

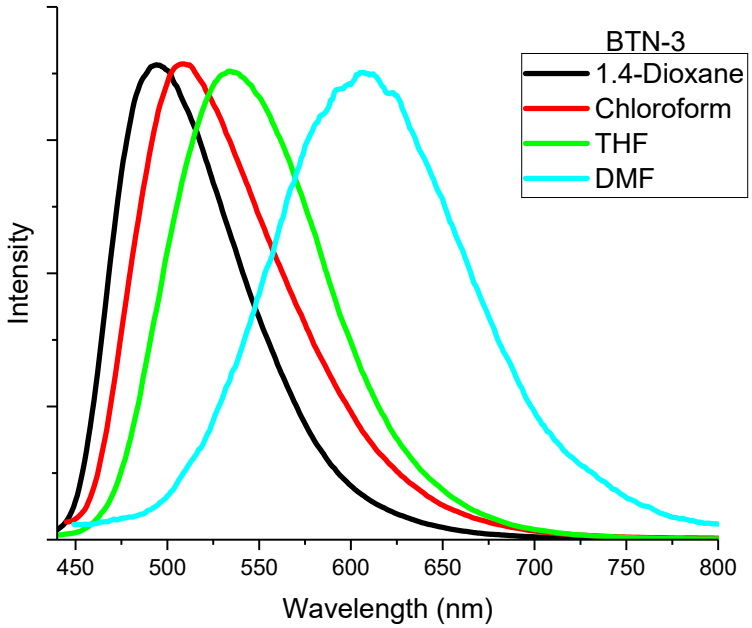


Fig. S6 Fluorescence emission spectra of the chromophores BTN-3 in solvents of varying polarity.

The fluorescence spectra of BTN-1, BTN-2 and BTN-3 were measured in a different diluted solution. As shown in Fig. S4-6. However, the fluorescent emission spectrum of BTN-1, BTN-2 and BTN-3 show significant red-shifts from low polarity to high polarity solvents (Fig. S4-6). The strong solvent polarity-dependent fluorescence indicates that BTN-1, BTN-2 and BTN-1 have a highly charged excited state due to photoinduced charge transfer.

3. Nonlinear data supplement

(Because the BTN-2 liner transmission index is too low, the nonlinear signal response is too weak to fit.)

To understand the nonlinear properties of the chromophores in the solution, there is an assumption of a particle non-interaction solution. Thus, the effective refractive nonlinearity in the pair-wise additive model can be expressed as:

$$n_{2,\,solution} = (1 - f)\, n_{2,\,solvent} + f\, n_{2,\,solute} \#(1)$$

where f is the molar fraction (the ratio of the amount of solute substance to the amount of solution substance) contained in the dilute solution, $n_{2,\,solvent}$ and $n_{2,\,solute}$ are the nonlinear refractive indices of the solvent and solute, respectively. Molar mass M_{DMF} = 73.09 g/mol, density ρ_{DMF} = 0.944 g/ml, $d_0 = 1 \times 10^{-5}$ mol/ml, $f = d_0/(d_0+\rho_{DMF}/M_{DMF})$ = 0.077 %.

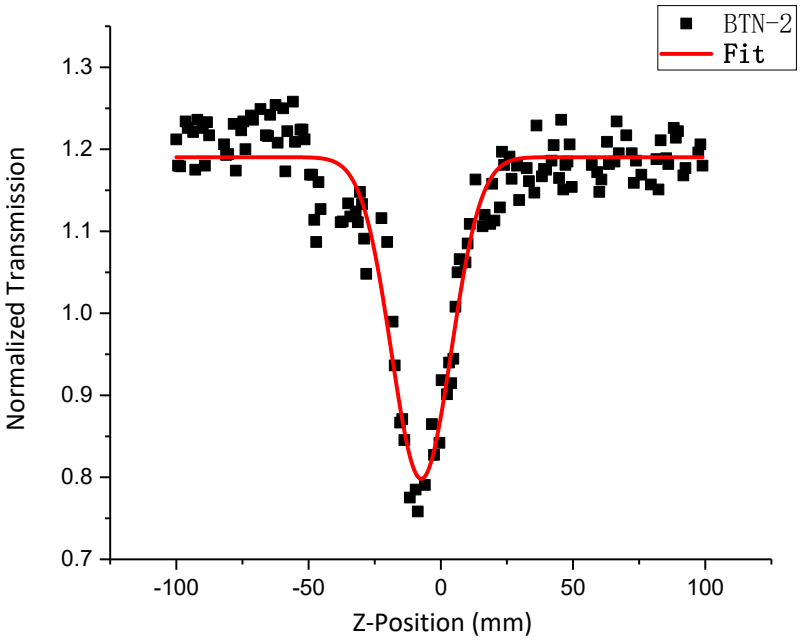


Fig. S7 Normalized closed-aperture Z-Scan curve of BTN-2.

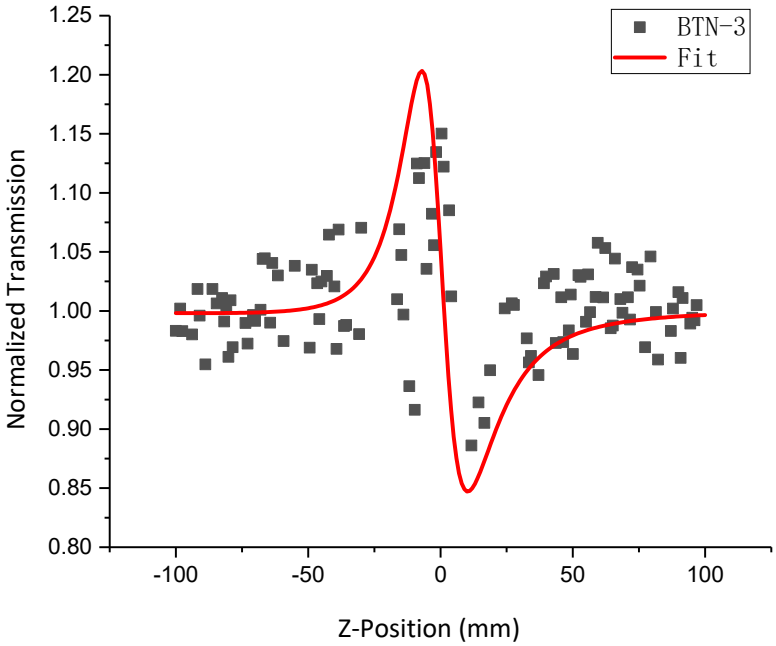


Fig. S8 Normalized closed-aperture Z-Scan curve of BTN-3.

4. Electrochemistry

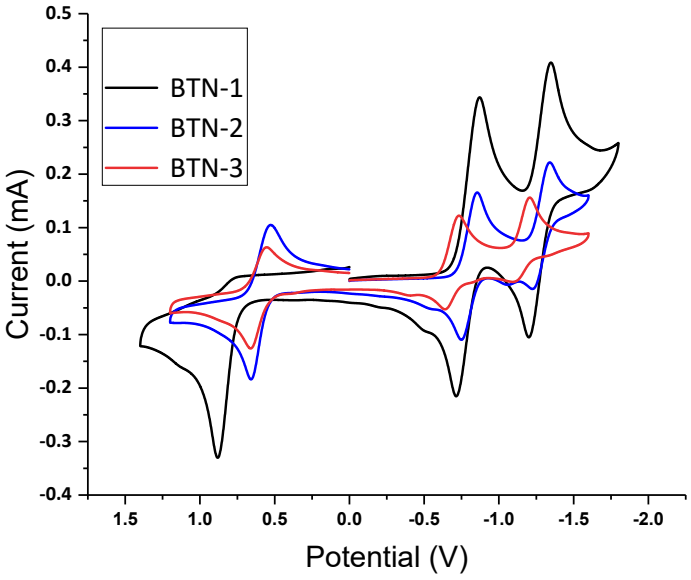


Fig. S9 Electrochemical spectra of BTN-1, BTN-2 and BTN-3.

Table S1 Electrochemical properties of BTN-3,BTN-4 and BTN-5.

Compound	E_{ox}^{onset} [a]	E_{red}^{onset} [a]	HOMO/LUMO (eV)[b]	HOMO/LUMO (eV)[d]	ΔE_g (eV)[c]	ΔE_g (eV)[d]
BTN-1	0.78	-1.27	-2.73 / -5.18	-3.33 / -5.53	2.45	2.20
BTN-2	0.60	-1.26	-2.74 / -5.00	-3.28 / -5.38	2.26	2.10
BTN-3	0.59	-1.15	-3.25 / -4.99	-3.09 / -5.31	1.74	1.96

[a] Measured in CH_2Cl_2 solution (glass carbon electrode with 0.1 M n-Bu_4NF_6 as the supporting electrolyte). The voltages are referenced to a SCE electrode.
[b] Calculated based on the respective onset oxidation and reduction potentials.
[c] HOMO and LUMO gap calculated based on the redox potentials: E_g = -e($E_{red}^{onset} - E_{ox}^{onset}$)eV.
[d] Calculated based on PBE1PBE/6-31G*.

From the energy levels calculated theoretically and projected electrochemically, the ΔE_g of the three chromophores are BTN-1 > BTN-2 > BTN-3 from small to large, which is consistent with the mechanism that the energy gap decreases with the growth of conjugation.

5. Computational Methodology and Calculation data

Unfortunately, due to the very low solubility of the three compounds, we only obtained crystals of BTN-1 and BTN-3, and the crystal data obtained was not usable because the points of the crystals were too weak. Therefore, all structural optimization calculations are performed by Gaussian 16W.

5.1 Theoretical calculation data summarized in tables

Table S2. The computed dipole moment of chromophores under vacuum and chloroform conditions

Chromophore	vacuum			polar medium ($CHCl_3$)		
	μ_g (D)	μ_e (D)	$\Delta\mu$ (D)	μ_g (D)	μ_e (D)	$\Delta\mu$ (D)
BTN-1	11.54	51.74	40.20	13.38	40.82	27.44

BTN-2	11.63	48.66	37.03	14.10	38.29	24.19
BTN-3	13.78	56.07	42.29	16.29	43.94	27.65

Table S3. Optical Absorption Properties (λ_{Max}, M_{ge} and E_{ge}) of the Intramolecular Charge Transfer.

	λ_{Max} (nm)[a]			μ_{ge} (D)[b]			E_{ge} (eV)[b]			M_{ge} (D)[c]		
	1.4-Dio	$CHCl_3$	DMF	1.4-Dio	$CHCl_3$	DMF	1.4-Diox	$CHCl_3$	DMF	1.4-Dio	$CHCl_3$	DMF
BTN-1	448	472	446	9.16	9.23	9.25	1.89	1.86	1.85	7.38	6.43	7.30
BTN-2	480	501	487	10.02	10.20	10.33	1.80	1.75	1.73	9.95	9.38	10.10
BTN-3	481	511	489	11.92	12.12	12.27	1.72	1.67	1.63	9.96	9.51	9.85

[a] Assigned to ICT excitation, and from UV-vis absorption in THF.

[b] Calculated by PBE1PBE/aug-cc-pVTZ

[c] Calculated from $$M_{ge}^2 = \frac{1500(hc)^2 \ln 10}{\pi N_A E_{ge}} \int \varepsilon_{ge}(v) dv$$

Comparing the theoretical calculations and the estimated transition dipole moment based on the UV-Vis ICT peak area, the size of the dipole moment is basically at a moderate level, so it is known that the impact of the transition dipole moment on the nonlinear response is not significant.

Table S4. Experimentally measured and theoretically calculated optical properties and frontier molecular orbita

	λ_{abs} (nm)[a]	λ_{max} (nm)[b]	$\Delta\lambda_{st}$ (nm)	$\Delta\lambda_{max}$ (nm)[c]	λ_{max} (nm)[d]	Oscillation strength, f[d]	Energy (ev)[d]	Selected major contributions[d]
BTN-1	327/457	472	15	16.8	665.79	0.52	1.86	H -> L, 99.1 %
					412.20	0.41	3.01	H-1 -> L, 93.6 %
					388.52	0.24	3.19	H -> L+1, 95.2 %
					353.74	0.79	3.51	H -> L+2, 91.6 %
BTN-2	334/360/482	497	15.2	25.2	706.50	0.58	1.75	H -> L, 99.2 %
					424.97	0.42	2.92	H-1 -> L, 90.7 %, H -> L, 5.7 %
					405.96	0.33	3.05	H -> L+1, 92.8 %, H -> L+2, 5.8 %
					376.60	0.57	3.29	H -> L+2 86.5 %, H-1 -> L 6.8 %, H -> L+1 5.3 %
BTN-3	338/380/503	533	30.6	39.2	744.38	0.81	1.67	H -> L, 99.4 %
					462.75	0.75	2.68	H-1 -> L, 90.8 %, H -> L+2, 6.2 %
					412.74	0.64	3.00	H -> L+1, 75.5 %, H -> L+2, 19.5 %
					388.77	0.16	3.18	H -> L+2 72.4%, H -> L+1 22.4%

[a] Experimentally measured UV absorption peaks
[b] Experimentally measured fluorescence emission peaks
[c] Calculated by PBE1PBE/aug-cc-pVTZ in solvents of varying polarity.
[d] Calculated by PBE1PBE/aug-cc-pVTZ under an applied electric field of single-linear state.

5.2 Optimized geometries and calculated energies,dipole moment, Mulliken charges.

BTN-1 Theoretical calculation data supplement：

Table 1. BTN-1 Optimization of ground state geometry in vacuum

Standard orientation:

Center	Atomic	Atomic	Coordinates (Angstroms)		
Number	Number	Type	X	Y	Z
1	6	0	5.372482	-1.873795	-0.324138
2	6	0	6.219177	-0.805277	-0.149716
3	6	0	5.660878	0.490356	0.078628
4	6	0	4.205283	0.618767	0.108488
5	6	0	3.336444	-0.514046	-0.084761
6	6	0	3.967483	-1.729822	-0.295964
7	7	0	6.301674	1.642168	0.295644
8	16	0	5.145413	2.785423	0.522174
9	7	0	3.796410	1.867930	0.355731
10	6	0	-5.786720	-1.184284	0.452195
11	6	0	-7.170001	-1.132218	0.444031
12	6	0	-7.855502	-0.000471	-0.062838
13	6	0	-7.073262	1.085010	-0.524827
14	6	0	-5.690475	1.022478	-0.512036
15	7	0	-9.231528	0.036643	-0.108067
16	6	0	-9.907123	1.293910	-0.434307
17	6	0	-10.007515	-1.006531	0.564358
18	6	0	-3.593889	-0.172010	-0.021961
19	6	0	-5.009049	-0.113766	-0.027259
20	6	0	1.870525	-0.406773	-0.046285
21	6	0	1.098848	-1.479214	0.443044
22	6	0	-0.285106	-1.423721	0.455427
23	6	0	-0.962172	-0.281142	-0.032612
24	6	0	-0.191829	0.789747	-0.520863
25	6	0	1.193132	0.732816	-0.520958
26	6	0	-2.377104	-0.219800	-0.026588
27	7	0	7.659470	-1.041000	-0.213277
28	8	0	8.407049	-0.070898	-0.128900
29	8	0	8.036607	-2.209383	-0.352022
30	1	0	5.814648	-2.846309	-0.501494
31	1	0	3.364156	-2.611381	-0.480924
32	1	0	-5.285954	-2.066306	0.842440
33	1	0	-7.723787	-1.980457	0.831466
34	1	0	-7.550931	1.979672	-0.899083
35	1	0	-5.114361	1.865975	-0.875702
36	1	0	-9.678469	2.112045	0.286700
37	1	0	-9.617729	1.649735	-1.451791
38	1	0	-10.985324	1.114445	-0.437161
39	1	0	-9.775396	-2.008582	0.138702

40	1	0	-9.818024	-1.046513	1.664244
41	1	0	-11.069309	-0.809879	0.396168
42	1	0	1.596054	-2.353105	0.852340
43	1	0	-0.862532	-2.247782	0.850859
44	1	0	-0.699464	1.669724	-0.901798
45	1	0	1.761342	1.572729	-0.898936

Standard basis: 6-31G(d) (6D, 7F)

SCF Done: E(RB3LYP) = -1615.55248267 a.u.

Thermal correction to Gibbs Free Energy = 0.278524 a.u.

Table 2 BTN-1 Calculation of excited state geometry in vacuum and dipole moments

Standard orientation

Center	Atomic	Atomic	Coordinates (Angstroms)		
Number	Number	Type	X	Y	Z
1	6	0	5.361551	-1.867296	-0.336899
2	6	0	6.208173	-0.804556	-0.155957
3	6	0	5.651638	0.486753	0.079402
4	6	0	4.204441	0.617339	0.109198
5	6	0	3.333047	-0.508030	-0.087864
6	6	0	3.959068	-1.721039	-0.306842
7	7	0	6.290699	1.634580	0.302310
8	16	0	5.143989	2.760904	0.529496
9	7	0	3.802530	1.864608	0.360785
10	6	0	-5.778473	-1.166597	0.480595
11	6	0	-7.159329	-1.111093	0.488505
12	6	0	-7.845785	0.022925	-0.000590
13	6	0	-7.066231	1.090475	-0.499637
14	6	0	-5.685860	1.024326	-0.502704
15	7	0	-9.216057	0.085276	0.009245
16	6	0	-9.889126	1.242629	-0.528651
17	6	0	-9.985376	-1.034801	0.494337
18	6	0	-3.589187	-0.165132	-0.019656
19	6	0	-5.003970	-0.103028	-0.013480
20	6	0	1.868770	-0.398750	-0.051139
21	6	0	1.100308	-1.463403	0.449202
22	6	0	-0.281561	-1.407843	0.463805
23	6	0	-0.957583	-0.278343	-0.032997
24	6	0	-0.190509	0.790201	-0.531366
25	6	0	1.192356	0.733602	-0.533370
26	6	0	-2.372497	-0.217301	-0.025430
27	7	0	7.642514	-1.042563	-0.220627
28	8	0	8.383474	-0.081032	-0.127383
29	8	0	8.011172	-2.201159	-0.368461
30	1	0	5.803923	-2.840016	-0.520688
31	1	0	3.352754	-2.600769	-0.497175

32	1	0	-5.277418	-2.050951	0.863301
33	1	0	-7.711546	-1.958389	0.878647
34	1	0	-7.544870	1.981486	-0.889551
35	1	0	-5.112006	1.860243	-0.891942
36	1	0	-9.613467	2.159767	0.009917
37	1	0	-9.663335	1.392696	-1.594238
38	1	0	-10.967492	1.109496	-0.429436
39	1	0	-9.805185	-1.945154	-0.095408
40	1	0	-9.757155	-1.259610	1.545314
41	1	0	-11.048036	-0.796513	0.427883
42	1	0	1.598212	-2.334157	0.866992
43	1	0	-0.857563	-2.233900	0.868976
44	1	0	-0.698304	1.667498	-0.919739
45	1	0	1.759502	1.571819	-0.920804

Ground to excited state transition electric dipole moments (Au):

state	X	Y	Z	Dip. S.	Osc.
1	2.9401	-0.0265	-0.0069	8.6447	0.4270
2	-2.0110	0.0662	0.0236	4.0489	0.3105
3	-2.2529	0.1508	0.0220	5.0989	0.4219
4	-0.0231	0.0133	-0.0058	0.0007	0.0001
5	2.5027	-0.0194	0.0378	6.2654	0.5685
6	-0.7885	-0.1013	0.0696	0.6368	0.0579
7	-0.1698	0.2423	0.0649	0.0918	0.0088
8	-0.0025	0.0075	0.0002	0.0001	0.0000
9	0.0140	0.0071	0.0015	0.0002	0.0000
10	0.0266	-0.0216	0.0495	0.0036	0.0004
11	0.0957	-1.0163	-0.2082	1.0854	0.1122
12	-0.0472	0.4677	-0.2570	0.2870	0.0305
13	0.0214	0.2575	-0.0137	0.0669	0.0071
14	0.4348	-0.1074	0.0320	0.2016	0.0217
15	0.9784	-0.1344	-0.0318	0.9764	0.1065
16	-0.8431	-0.2221	-0.0396	0.7617	0.0884
17	0.3071	0.2175	0.0382	0.1431	0.0168
18	-0.4168	0.1812	0.0357	0.2078	0.0247
19	-0.0833	0.3492	0.0529	0.1317	0.0159
20	-0.0582	0.0244	0.0136	0.0042	0.0005
21	-0.0363	-0.0059	-0.0029	0.0014	0.0002
22	-0.5172	0.1053	0.0129	0.2787	0.0346
23	0.0280	-0.3187	0.0910	0.1107	0.0140
24	0.0037	-0.0592	0.0553	0.0066	0.0008
25	0.2144	-0.0758	-0.0503	0.0543	0.0069
26	0.0234	0.0085	-0.0172	0.0009	0.0001
27	-0.0139	-0.3598	0.1632	0.1563	0.0206
28	0.0676	-0.0053	0.0231	0.0051	0.0007
29	-0.1434	-0.5829	-0.1188	0.3745	0.0499
30	-0.0003	0.1662	0.3812	0.1730	0.0235
31	0.2054	0.1819	0.0435	0.0772	0.0105
32	-0.0137	0.0618	0.0333	0.0051	0.0007
33	0.0196	0.3826	-0.1682	0.1751	0.0240
34	-0.0316	0.0208	-0.0591	0.0049	0.0007
35	0.1049	-0.0047	-0.0149	0.0113	0.0016

36	0.0230	0.0111	0.0165	0.0009	0.0001
37	0.3216	0.0644	0.0695	0.1124	0.0157
38	-0.0625	-0.1837	-0.2909	0.1223	0.0173
39	0.2004	-0.0261	-0.1454	0.0620	0.0088
40	0.0595	-0.1394	-0.0408	0.0246	0.0035

Standard basis:TZVP (5D, 7F)

SCF Done: E(RPBE1PBE) = -1614.29472680 a.u.

Table 3. BTN-1 Optimization of Ground State Geometry in Chloroform Solvent and Mulliken charges

Standard orientation:

Center	Atomic	Atomic	Coordinates (Angstroms)		
Number	Number	Type	X	Y	Z
1	6	0	5.372482	-1.873795	-0.324138
2	6	0	6.219177	-0.805277	-0.149716
3	6	0	5.660878	0.490356	0.078628
4	6	0	4.205283	0.618767	0.108488
5	6	0	3.336444	-0.514046	-0.084761
6	6	0	3.967483	-1.729822	-0.295964
7	7	0	6.301674	1.642168	0.295644
8	16	0	5.145413	2.785423	0.522174
9	7	0	3.796410	1.867930	0.355731
10	6	0	-5.786720	-1.184284	0.452195
11	6	0	-7.170001	-1.132218	0.444031
12	6	0	-7.855502	-0.000471	-0.062838
13	6	0	-7.073262	1.085010	-0.524827
14	6	0	-5.690475	1.022478	-0.512036
15	7	0	-9.231528	0.036643	-0.108067
16	6	0	-9.907123	1.293910	-0.434307
17	6	0	-10.007515	-1.006531	0.564358
18	6	0	-3.593889	-0.172010	-0.021961
19	6	0	-5.009049	-0.113766	-0.027259
20	6	0	1.870525	-0.406773	-0.046285
21	6	0	1.098848	-1.479214	0.443044
22	6	0	-0.285106	-1.423721	0.455427
23	6	0	-0.962172	-0.281142	-0.032612
24	6	0	-0.191829	0.789747	-0.520863
25	6	0	1.193132	0.732816	-0.520958
26	6	0	-2.377104	-0.219800	-0.026588
27	7	0	7.659470	-1.041000	-0.213277
28	8	0	8.407049	-0.070898	-0.128900
29	8	0	8.036607	-2.209383	-0.352022
30	1	0	5.814648	-2.846309	-0.501494
31	1	0	3.364156	-2.611381	-0.480924
32	1	0	-5.285954	-2.066306	0.842440
33	1	0	-7.723787	-1.980457	0.831466
34	1	0	-7.550931	1.979672	-0.899083
35	1	0	-5.114361	1.865975	-0.875702
36	1	0	-9.678469	2.112045	0.286700
37	1	0	-9.617729	1.649735	-1.451791
38	1	0	-10.985324	1.114445	-0.437161
39	1	0	-9.775396	-2.008582	0.138702
40	1	0	-9.818024	-1.046513	1.664244
41	1	0	-11.069309	-0.809879	0.396168
42	1	0	1.596054	-2.353105	0.852340
43	1	0	-0.862532	-2.247782	0.850859
44	1	0	-0.699464	1.669724	-0.901798

45	1	0	1.761342	1.572729	-0.898936

Mulliken charges:

1	C	-0.191496	24	C	-0.179525
2	C	0.284787	25	C	-0.187029
3	C	0.230319	26	C	-0.080153
4	C	0.175875	27	N	0.359990
5	C	0.118480	28	O	-0.398473
6	C	-0.252542	29	O	-0.420481
7	N	-0.561391	30	H	0.241852
8	S	0.648934	31	H	0.215042
9	N	-0.581953	32	H	0.190953
10	C	-0.172583	33	H	0.187203
11	C	-0.245740	34	H	0.187504
12	C	0.375341	35	H	0.191328
13	C	-0.244584	36	H	0.189380
14	C	-0.171234	37	H	0.196351
15	N	-0.514209	38	H	0.200268
16	C	-0.389169	39	H	0.197288
17	C	-0.388624	40	H	0.188538
18	C	-0.058825	41	H	0.200575
19	C	-0.031225	42	H	0.197355
20	C	0.065223	43	H	0.199038
21	C	-0.207415	44	H	0.198574
22	C	-0.175021	45	H	0.208180
23	C	0.003294			

Standard basis: 6-31G(d) (6D, 7F)

SCF Done: E(RPBE1PBE) = -1613.92365189 a.u.

Table 4. BTN-1 Calculation of excited state geometry in chloroform solvent and dipole moments

Standard orientation:

Center	Atomic	Atomic	Coordinates (Angstroms)		
Number	Number	Type	X	Y	Z
1	6	0	5.361551	-1.867296	-0.336899
2	6	0	6.208173	-0.804556	-0.155957
3	6	0	5.651638	0.486753	0.079402
4	6	0	4.204441	0.617339	0.109198
5	6	0	3.333047	-0.508030	-0.087864
6	6	0	3.959068	-1.721039	-0.306842
7	7	0	6.290699	1.634580	0.302310
8	16	0	5.143989	2.760904	0.529496
9	7	0	3.802530	1.864608	0.360785
10	6	0	-5.778473	-1.166597	0.480595
11	6	0	-7.159329	-1.111093	0.488505
12	6	0	-7.845785	0.022925	-0.000590
13	6	0	-7.066231	1.090475	-0.499637
14	6	0	-5.685860	1.024326	-0.502704
15	7	0	-9.216057	0.085276	0.009245
16	6	0	-9.889126	1.242629	-0.528651

17	6	0	-9.985376	-1.034801	0.494337
18	6	0	-3.589187	-0.165132	-0.019656
19	6	0	-5.003970	-0.103028	-0.013480
20	6	0	1.868770	-0.398750	-0.051139
21	6	0	1.100308	-1.463403	0.449202
22	6	0	-0.281561	-1.407843	0.463805
23	6	0	-0.957583	-0.278343	-0.032997
24	6	0	-0.190509	0.790201	-0.531366
25	6	0	1.192356	0.733602	-0.533370
26	6	0	-2.372497	-0.217301	-0.025430
27	7	0	7.642514	-1.042563	-0.220627
28	8	0	8.383474	-0.081032	-0.127383
29	8	0	8.011172	-2.201159	-0.368461
30	1	0	5.803923	-2.840016	-0.520688
31	1	0	3.352754	-2.600769	-0.497175
32	1	0	-5.277418	-2.050951	0.863301
33	1	0	-7.711546	-1.958389	0.878647
34	1	0	-7.544870	1.981486	-0.889551
35	1	0	-5.112006	1.860243	-0.891942
36	1	0	-9.613467	2.159767	0.009917
37	1	0	-9.663335	1.392696	-1.594238
38	1	0	-10.967492	1.109496	-0.429436
39	1	0	-9.805185	-1.945154	-0.095408
40	1	0	-9.757155	-1.259610	1.545314
41	1	0	-11.048036	-0.796513	0.427883
42	1	0	1.598212	-2.334157	0.866992
43	1	0	-0.857563	-2.233900	0.868976
44	1	0	-0.698304	1.667498	-0.919739
45	1	0	1.759502	1.571819	-0.920804

Ground to excited state transition electric dipole moments (Au):

state	X	Y	Z	Dip. S.	Osc.
1	3.3916	-0.0546	-0.0117	11.5061	0.5249
2	-2.3679	0.1001	0.0312	5.6177	0.4140
3	-1.7467	0.1897	0.0323	3.0881	0.2414
4	3.0367	-0.0132	0.0178	9.2221	0.7919
5	-0.0536	-0.0762	0.0671	0.0132	0.0012
6	-0.0091	-0.1017	0.0690	0.0152	0.0014
7	-0.5575	0.3835	0.0902	0.4660	0.0438
8	0.0074	-0.0256	0.0065	0.0007	0.0001
9	0.0075	0.0353	0.0086	0.0014	0.0001
10	-0.0394	-1.2250	-0.2410	1.5604	0.1555
11	0.0377	-0.0167	0.0481	0.0040	0.0004
12	0.8673	-0.1760	-0.0358	0.7845	0.0822
13	0.0478	-0.6375	0.2979	0.4975	0.0522
14	0.2033	0.0141	0.0494	0.0439	0.0047
15	-0.0136	-0.0689	0.0047	0.0050	0.0005
16	-1.2135	-0.1417	-0.0201	1.4931	0.1709
17	0.2012	0.1636	0.0314	0.0682	0.0079
18	-0.3998	0.2392	0.0351	0.2183	0.0255
19	0.5513	-0.2042	-0.0277	0.3464	0.0420
20	0.2203	-0.2789	-0.0277	0.1271	0.0158
21	0.0552	0.1611	-0.0939	0.0378	0.0047
22	-0.0410	-0.1013	0.0362	0.0133	0.0017
23	0.0658	0.1040	-0.0318	0.0162	0.0020
24	-0.0349	0.1371	0.0726	0.0253	0.0032

25	0.1035	0.0634	0.1121	0.0273	0.0035
26	0.0050	0.2297	-0.1099	0.0649	0.0084
27	-0.2250	-0.8927	-0.1321	0.8651	0.1119
28	0.0193	0.0761	-0.0113	0.0063	0.0008
29	-0.0799	-0.1616	-0.0372	0.0339	0.0044
30	-0.0226	-0.5308	0.2392	0.3395	0.0450
31	0.1429	0.1685	0.0379	0.0502	0.0067
32	-0.0677	0.0301	0.0062	0.0055	0.0007
33	0.1050	0.0034	-0.0063	0.0111	0.0015
34	0.2827	0.0323	0.0334	0.0821	0.0113
35	0.2665	0.0719	0.1301	0.0931	0.0130
36	0.0214	-0.0585	-0.3270	0.1108	0.0156
37	0.0797	0.0998	0.0091	0.0164	0.0023
38	-0.0798	0.1183	0.1729	0.0503	0.0071
39	-0.0121	0.1932	0.4526	0.2423	0.0343
40	-0.3477	0.0797	0.0492	0.1297	0.0186

Standard basis: TZVP (5D, 7F)

SCF Done:E(RPBE1PBE) = -1614.30781131 a.u.

BTN-2 Theoretical calculation data supplement：

Table 5. BTN-2 Optimization of ground state geometry in vacuum

Standard orientation:

Center	Atomic	Atomic	Coordinates (Angstroms)		
Number	Number	Type	X	Y	Z
1	6	0	1.808879	-0.578643	0.017038
2	6	0	1.094771	-1.686173	0.315130
3	6	0	-0.247645	-1.717091	0.346745
4	6	0	-0.998865	-0.635662	0.068569
5	6	0	-0.306050	0.472304	-0.247194
6	6	0	1.037511	0.490993	-0.270135
7	6	0	-2.346227	-0.730106	0.114698
8	6	0	-3.247483	0.240140	-0.132455
9	6	0	-4.595082	0.147295	-0.087147
10	6	0	-5.341922	1.231657	-0.368846
11	6	0	-6.684303	1.205081	-0.341882
12	6	0	-7.391600	0.098215	-0.032232
13	6	0	-6.630834	-0.980999	0.248236
14	6	0	-5.287523	-0.963085	0.223203
15	7	0	-8.673625	0.074579	-0.006846
16	6	0	-9.379903	-1.185178	0.345763
17	6	0	-9.439217	1.307269	-0.330303
18	6	0	3.170586	-0.568451	-0.007260
19	6	0	3.862474	-1.719112	-0.152227
20	6	0	5.201096	-1.782827	-0.217913
21	6	0	5.980005	-0.689308	-0.132067
22	6	0	5.312503	0.472914	0.034132
23	6	0	3.957713	0.529012	0.095099
24	7	0	5.884182	1.598709	0.158201
25	16	0	4.776322	2.865842	0.384929
26	7	0	3.536368	1.707971	0.298189
27	7	0	7.233365	-0.800895	-0.206913
28	8	0	8.080945	0.199784	-0.138563
29	8	0	7.834934	-1.959194	-0.368400
30	1	0	1.572498	-2.635715	0.603712
31	1	0	-0.726333	-2.673528	0.624903

32	1	0	-0.813228	1.410539	-0.522512
33	1	0	1.462527	1.446456	-0.609193
34	1	0	-2.740508	-1.721811	0.387760
35	1	0	-2.852177	1.231654	-0.404661
36	1	0	-4.861024	2.190186	-0.634955
37	1	0	-7.172064	2.160641	-0.592872
38	1	0	-7.075821	-1.952531	0.517322
39	1	0	-4.782310	-1.909777	0.471365
40	1	0	-9.168002	-1.991690	-0.392696
41	1	0	-9.138694	-1.510925	1.383174
42	1	0	-10.482606	-1.039721	0.324904
43	1	0	-9.228428	2.121242	0.400182
44	1	0	-9.250850	1.641454	-1.375975
45	1	0	-10.534092	1.121274	-0.266651
46	1	0	3.365538	-2.693036	-0.285371
47	1	0	5.642048	-2.784922	-0.363739

Standard basis: 6-31G(d) (6D, 7F)

SCF Done: E(RB3LYP) = -1616.61870359 a.u.

Thermal correction to Gibbs Free Energy = 0.302386 a.u.

Table 6. BTN-2 Calculation of excited state geometry in vacuum and dipole moments

Standard orientation:

Center	Atomic	Atomic	Coordinates (Angstroms)		
Number	Number	Type	X	Y	Z
1	6	0	1.839197	-0.579703	0.021578
2	6	0	1.154066	-1.704405	0.507519
3	6	0	-0.228589	-1.732899	0.555353
4	6	0	-1.003884	-0.646535	0.113598
5	6	0	-0.311093	0.478772	-0.369256
6	6	0	1.070568	0.516392	-0.408318
7	6	0	-2.453761	-0.741339	0.184778
8	6	0	-3.341923	0.196738	-0.207291
9	6	0	-4.790783	0.122135	-0.144921
10	6	0	-5.556881	1.197328	-0.621175
11	6	0	-6.940223	1.193728	-0.592558
12	6	0	-7.648026	0.087327	-0.078359
13	6	0	-6.883397	-0.996249	0.412003
14	6	0	-5.502900	-0.972531	0.374391
15	7	0	-9.021070	0.060821	-0.055371
16	6	0	-9.709135	-1.040374	0.573825
17	6	0	-9.766297	1.224795	-0.469193
18	6	0	3.304421	-0.588014	-0.054966
19	6	0	4.006053	-1.752212	-0.311468
20	6	0	5.413175	-1.802551	-0.379957
21	6	0	6.191899	-0.687957	-0.202462
22	6	0	5.555972	0.558645	0.069942
23	6	0	4.104271	0.590473	0.139556
24	7	0	6.122352	1.743295	0.296413
25	16	0	4.909106	2.785892	0.573865
26	7	0	3.626824	1.803439	0.424230
27	7	0	7.635735	-0.827459	-0.308307
28	8	0	8.313800	0.179423	-0.211816
29	8	0	8.077447	-1.955396	-0.491457
30	1	0	1.715415	-2.553556	0.887953
31	1	0	-0.730504	-2.612280	0.952398

32	1	0	-0.863093	1.344608	-0.722708
33	1	0	1.568355	1.402418	-0.784747
34	1	0	-2.825582	-1.677976	0.598394
35	1	0	-2.961532	1.128647	-0.625517
36	1	0	-5.045939	2.068528	-1.026499
37	1	0	-7.473113	2.058330	-0.971587
38	1	0	-7.376841	-1.866547	0.829789
39	1	0	-4.964890	-1.831645	0.765913
40	1	0	-9.464885	-1.994841	0.089425
41	1	0	-9.467222	-1.129374	1.643583
42	1	0	-10.786047	-0.889840	0.482122
43	1	0	-9.548583	2.104651	0.154816
44	1	0	-9.550791	1.487201	-1.513272
45	1	0	-10.834194	1.012894	-0.395137
46	1	0	3.455649	-2.667762	-0.502485
47	1	0	5.914850	-2.739992	-0.592576

Ground to excited state transition electric dipole moments (Au):

state	X	Y	Z	Dip. S.	Osc.
1	3.1219	-0.0087	-0.0100	9.7466	0.4660
2	-2.2060	0.0169	0.0400	4.8684	0.3667
3	-2.6410	0.2023	0.0130	7.0157	0.5613
4	-0.1827	0.0238	-0.0124	0.0341	0.0029
5	-1.9468	0.0417	-0.0379	3.7932	0.3274
6	0.1599	0.0999	-0.0638	0.0396	0.0036
7	-0.4134	0.1500	0.0946	0.2024	0.0193
8	0.0717	-0.0151	0.0052	0.0054	0.0005
9	0.0423	-0.0119	0.0513	0.0046	0.0005
10	-0.1537	-0.7696	-0.2859	0.6977	0.0719
11	-0.4581	0.8128	-0.1387	0.8897	0.0927
12	0.4371	0.0445	0.0583	0.1964	0.0207
13	0.9721	-0.2510	-0.0087	1.0081	0.1076
14	0.7254	-0.0679	-0.0142	0.5310	0.0571
15	0.5702	0.0125	0.1057	0.3365	0.0379
16	-0.0590	0.2326	0.0448	0.0596	0.0069
17	-0.0375	0.2691	0.0241	0.0744	0.0086
18	0.0662	0.3645	0.0641	0.1414	0.0170
19	-0.0289	0.0334	-0.0033	0.0020	0.0002
20	0.3709	-0.1190	-0.0648	0.1559	0.0189
21	0.2853	-0.3474	0.1002	0.2121	0.0262
22	0.0757	-0.0195	-0.0610	0.0098	0.0012
23	0.0653	-0.0212	0.0499	0.0072	0.0009
24	0.4605	-0.4798	0.1975	0.4812	0.0614
25	0.0798	-0.0735	0.0236	0.0123	0.0016
26	0.1078	-0.0033	0.0113	0.0118	0.0015
27	-0.3412	0.4467	0.0243	0.3166	0.0418
28	-0.3025	-0.3646	0.0513	0.2271	0.0304
29	0.1804	0.3231	0.3914	0.2901	0.0389
30	0.2303	-0.1734	0.1013	0.0934	0.0126
31	0.2656	-0.0386	-0.0569	0.0753	0.0103
32	0.0116	-0.0191	-0.0608	0.0042	0.0006
33	-0.4289	-0.0786	-0.2375	0.2465	0.0341
34	0.0125	0.0282	-0.0689	0.0057	0.0008
35	0.1293	0.0638	0.0113	0.0209	0.0029
36	0.1154	-0.2306	0.1949	0.1045	0.0147
37	0.0924	-0.4884	-0.0299	0.2480	0.0354

38	0.2892	-0.1535	-0.0266	0.1079	0.0154
39	0.1616	-0.5672	-0.0223	0.3483	0.0502
40	0.3510	-0.2760	-0.0226	0.1999	0.0292

Standard basis: TZVP (5D, 7F)

SCF Done: E(RPBE1PBE) = -1615.54111796 a.u.

Table 7. BTN-2 Optimization of Ground State Geometry in Chloroform Solvent and Mulliken charges

Standard orientation:

Center	Atomic	Atomic	Coordinates (Angstroms)		
Number	Number	Type	X	Y	Z
1	6	0	1.839483	-0.579486	0.035037
2	6	0	1.155212	-1.700340	0.533616
3	6	0	-0.227636	-1.727048	0.585546
4	6	0	-1.003491	-0.644574	0.131600
5	6	0	-0.311584	0.475532	-0.367633
6	6	0	1.070366	0.512043	-0.408576
7	6	0	-2.453262	-0.739089	0.203924
8	6	0	-3.340534	0.194708	-0.205230
9	6	0	-4.789223	0.121479	-0.144302
10	6	0	-5.554004	1.189348	-0.643075
11	6	0	-6.937652	1.186206	-0.618427
12	6	0	-7.648009	0.088081	-0.084866
13	6	0	-6.883939	-0.987574	0.428801
14	6	0	-5.503109	-0.964830	0.394040
15	7	0	-9.018241	0.061248	-0.066638
16	6	0	-9.709476	-1.029177	0.581816
17	6	0	-9.764128	1.216700	-0.508552
18	6	0	3.303747	-0.589673	-0.045340
19	6	0	4.001558	-1.755944	-0.307448
20	6	0	5.406318	-1.806034	-0.388783
21	6	0	6.186920	-0.689404	-0.217114
22	6	0	5.554458	0.556854	0.066664
23	6	0	4.105456	0.587708	0.150306
24	7	0	6.119740	1.742346	0.295520
25	16	0	4.911721	2.786302	0.596066
26	7	0	3.633264	1.798689	0.453940
27	7	0	7.626693	-0.825427	-0.337911
28	8	0	8.312203	0.179121	-0.247389
29	8	0	8.080730	-1.948285	-0.526881
30	1	0	1.716083	-2.547269	0.919399
31	1	0	-0.728495	-2.602324	0.992591
32	1	0	-0.863317	1.336086	-0.734330
33	1	0	1.566687	1.390983	-0.803539
34	1	0	-2.824718	-1.669691	0.631531
35	1	0	-2.959769	1.119616	-0.638939
36	1	0	-5.041925	2.052912	-1.063298
37	1	0	-7.469404	2.043553	-1.015075
38	1	0	-7.378677	-1.849830	0.861413
39	1	0	-4.966951	-1.817238	0.802843
40	1	0	-9.462752	-1.993056	0.118599
41	1	0	-9.472229	-1.095543	1.653702
42	1	0	-10.785449	-0.880477	0.482316
43	1	0	-9.550669	2.108503	0.098826
44	1	0	-9.544331	1.458686	-1.556302
45	1	0	-10.831404	1.004124	-0.434852
46	1	0	3.451231	-2.671900	-0.495059

47	1	0	5.900079	-2.745565	-0.609126

Mulliken charges:

1	C	0.054657	25	S	0.647177
2	C	-0.201646	26	N	-0.575990
3	C	-0.245899	27	N	0.371758
4	C	0.140146	28	O	-0.404577
5	C	-0.231476	29	O	-0.425595
6	C	-0.182680	30	H	0.192505
7	C	-0.239251	31	H	0.187188
8	C	-0.214191	32	H	0.188142
9	C	0.116594	33	H	0.202460
10	C	-0.243895	34	H	0.175440
11	C	-0.241941	35	H	0.178628
12	C	0.368962	36	H	0.180200
13	C	-0.240714	37	H	0.183376
14	C	-0.225726	38	H	0.183831
15	N	-0.508542	39	H	0.181616
16	C	-0.390425	40	H	0.195273
17	C	-0.390489	41	H	0.190142
18	C	0.123324	42	H	0.199073
19	C	-0.256142	43	H	0.190042
20	C	-0.194193	44	H	0.195245
21	C	0.283206	45	H	0.198858
22	C	0.224821	46	H	0.211858
23	C	0.166611	47	H	0.239348
24	N	-0.557108			

Standard basis: 6-31G(d) (6D, 7F)

SCF Done: E(RPBE1PBE) = -1615.17170929 a.u.

Table 8. BTN-2 Calculation of excited state geometry in chloroform solvent and dipole moments

Standard orientation:

Center	Atomic	Atomic	Coordinates (Angstroms)		
Number	Number	Type	X	Y	Z
1	6	0	1.839197	-0.579703	0.021578
2	6	0	1.154066	-1.704405	0.507519
3	6	0	-0.228589	-1.732899	0.555353
4	6	0	-1.003884	-0.646535	0.113598
5	6	0	-0.311093	0.478772	-0.369256
6	6	0	1.070568	0.516392	-0.408318
7	6	0	-2.453761	-0.741339	0.184778
8	6	0	-3.341923	0.196738	-0.207291
9	6	0	-4.790783	0.122135	-0.144921
10	6	0	-5.556881	1.197328	-0.621175
11	6	0	-6.940223	1.193728	-0.592558
12	6	0	-7.648026	0.087327	-0.078359
13	6	0	-6.883397	-0.996249	0.412003
14	6	0	-5.502900	-0.972531	0.374391

15	7	0	-9.021070	0.060821	-0.055371
16	6	0	-9.709135	-1.040374	0.573825
17	6	0	-9.766297	1.224795	-0.469193
18	6	0	3.304421	-0.588014	-0.054966
19	6	0	4.006053	-1.752212	-0.311468
20	6	0	5.413175	-1.802551	-0.379957
21	6	0	6.191899	-0.687957	-0.202462
22	6	0	5.555972	0.558645	0.069942
23	6	0	4.104271	0.590473	0.139556
24	7	0	6.122352	1.743295	0.296413
25	16	0	4.909106	2.785892	0.573865
26	7	0	3.626824	1.803439	0.424230
27	7	0	7.635735	-0.827459	-0.308307
28	8	0	8.313800	0.179423	-0.211816
29	8	0	8.077447	-1.955396	-0.491457
30	1	0	1.715415	-2.553556	0.887953
31	1	0	-0.730504	-2.612280	0.952398
32	1	0	-0.863093	1.344608	-0.722708
33	1	0	1.568355	1.402418	-0.784747
34	1	0	-2.825582	-1.677976	0.598394
35	1	0	-2.961532	1.128647	-0.625517
36	1	0	-5.045939	2.068528	-1.026499
37	1	0	-7.473113	2.058330	-0.971587
38	1	0	-7.376841	-1.866547	0.829789
39	1	0	-4.964890	-1.831645	0.765913
40	1	0	-9.464885	-1.994841	0.089425
41	1	0	-9.467222	-1.129374	1.643583
42	1	0	-10.786047	-0.889840	0.482122
43	1	0	-9.548583	2.104651	0.154816
44	1	0	-9.550791	1.487201	-1.513272
45	1	0	-10.834194	1.012894	-0.395137
46	1	0	3.455649	-2.667762	-0.502485
47	1	0	5.914850	-2.739992	-0.592576

Ground to excited state transition electric dipole moments (Au):

state	X	Y	Z	Dip. S.	Osc.
1	3.6855	-0.0362	-0.0141	13.5842	0.5840
2	-2.4230	0.0293	0.0454	5.8736	0.4198
3	-2.0805	0.2382	0.0329	4.3863	0.3282
4	2.6497	-0.1320	0.0536	7.0413	0.5679
5	-0.0589	-0.1153	0.0722	0.0220	0.0019
6	0.0635	-0.0661	0.0259	0.0091	0.0008
7	0.6953	-0.2295	-0.1297	0.5529	0.0511
8	0.0968	-0.0151	-0.0200	0.0100	0.0009
9	-0.0757	-1.1661	-0.2840	1.4462	0.1441
10	0.8787	-0.7157	0.1911	1.3208	0.1355
11	0.5622	0.2410	-0.1613	0.4002	0.0412
12	0.0895	-0.0556	0.0497	0.0136	0.0014
13	0.4179	0.0363	0.0303	0.1769	0.0184
14	0.0771	-0.0909	-0.0012	0.0142	0.0015
15	-0.9960	0.1224	-0.1124	1.0196	0.1123
16	-0.0906	0.2956	0.0518	0.0983	0.0111
17	-0.0653	0.1190	0.0045	0.0184	0.0021
18	0.4412	-0.2478	-0.0475	0.2583	0.0305
19	-0.3249	0.2926	-0.0070	0.1912	0.0233
20	0.0109	0.1551	-0.1278	0.0405	0.0050

21	0.0502	-0.1205	0.0055	0.0171	0.0021
22	-0.4180	0.5131	-0.2238	0.4881	0.0612
23	0.1678	-0.0654	0.0762	0.0383	0.0048
24	-0.0217	-0.0319	-0.0270	0.0022	0.0003
25	-0.0936	0.2799	0.0559	0.0902	0.0115
26	-0.2145	0.2615	-0.1211	0.1291	0.0166
27	-0.0633	-0.9020	-0.1016	0.8279	0.1068
28	0.0769	0.1426	0.0438	0.0281	0.0037
29	-0.3875	-0.1796	-0.1443	0.2032	0.0267
30	0.0622	0.0667	0.0528	0.0111	0.0015
31	-0.3417	0.1838	0.0487	0.1529	0.0209
32	0.1975	0.0312	0.0468	0.0422	0.0058
33	0.4440	0.0373	0.0605	0.2021	0.0277
34	-0.2049	0.0694	-0.4957	0.2926	0.0405
35	0.0197	0.2208	0.2878	0.1320	0.0184
36	-0.0267	-0.0364	0.0200	0.0024	0.0003
37	0.3086	-0.9008	-0.0078	0.9067	0.1283
38	-0.1274	-0.2536	0.0186	0.0809	0.0115
39	-0.1783	0.1297	0.0068	0.0487	0.0070
40	-0.3399	0.2686	-0.0007	0.1877	0.0270

Standard basis: TZVP (5D, 7F)

SCF Done: E(RPBE1PBE) = -1615.55439277 a.u.

BTN-3 Theoretical calculation data supplement：

Table 9. BTN-3 Optimization of ground state geometry in vacuum

Standard orientation:

Center	Atomic	Atomic	Coordinates (Angstroms)		
Number	Number	Type	X	Y	Z
1	6	0	-6.826228	-1.792691	0.001813
2	6	0	-7.528823	-0.606668	0.001769
3	6	0	-6.809099	0.631810	0.001082
4	6	0	-5.352518	0.576162	0.000454
5	6	0	-4.642146	-0.680208	0.000511
6	6	0	-5.416111	-1.836424	0.001203
7	7	0	-7.288065	1.879327	0.000913
8	16	0	-5.984090	2.877956	0.000106
9	7	0	-4.768430	1.775080	-0.000173
10	6	0	-0.599990	-0.749746	0.003908
11	6	0	0.122725	-1.961388	-0.001561
12	6	0	1.508270	-1.951586	-0.002205
13	6	0	2.244299	-0.746155	-0.002587
14	6	0	1.509406	0.461860	0.002886
15	6	0	0.125914	0.464024	0.008707
16	6	0	-2.015150	-0.740578	0.004543
17	6	0	3.700029	-0.811689	-0.003243
18	6	0	-3.234280	-0.711415	0.005084
19	6	0	4.559327	0.235235	0.001698
20	6	0	6.013870	0.190490	-0.009363
21	6	0	6.742371	1.395687	-0.014706
22	6	0	8.128650	1.427789	-0.030922
23	6	0	8.881127	0.229255	-0.057455
24	6	0	8.154736	-0.989295	-0.031292
25	6	0	6.770432	-0.999522	-0.015076
26	7	0	10.260837	0.242889	-0.110116
27	6	0	11.003914	-1.005373	0.076922

28	6	0	10.975242	1.507658	0.072047
29	7	0	-8.988964	-0.666970	0.002421
30	8	0	-9.610336	0.392477	0.002239
31	8	0	-9.511804	-1.787062	0.003027
32	1	0	-7.395251	-2.714501	0.002348
33	1	0	-4.920399	-2.800959	0.001273
34	1	0	-0.418473	-2.902605	-0.006475
35	1	0	2.047405	-2.895790	-0.007611
36	1	0	2.032029	1.413265	0.007779
37	1	0	-0.420247	1.402246	0.008894
38	1	0	4.104908	-1.822432	-0.019125
39	1	0	4.146840	1.243650	0.012417
40	1	0	6.199442	2.338591	0.001289
41	1	0	8.628313	2.389081	-0.025783
42	1	0	8.680424	-1.936753	-0.026453
43	1	0	6.265442	-1.961333	0.000615
44	1	0	10.835931	-1.472526	1.080474
45	1	0	10.731068	-1.753542	-0.697458
46	1	0	12.072748	-0.786454	-0.032839
47	1	0	10.682335	2.245530	-0.707304
48	1	0	10.797698	1.974433	1.070534
49	1	0	12.048901	1.313798	-0.043029

Standard basis: 6-31G(d) (6D, 7F)

SCF Done: E(RB3LYP) = -1692.96375710 a.u.

Thermal correction to Gibbs Free Energy = 0.307574

Table 10. BTN-3 Calculation of excited state geometry in vacuum and dipole moments

Standard orientation:

Center	Atomic	Atomic	Coordinates (Angstroms)		
Number	Number	Type	X	Y	Z
1	6	0	-6.813856	-1.784072	-0.000925
2	6	0	-7.507057	-0.597568	0.001797
3	6	0	-6.782687	0.631746	0.003487
4	6	0	-5.334836	0.568522	0.002255
5	6	0	-4.632419	-0.685110	-0.000588
6	6	0	-5.407117	-1.835319	-0.002112
7	7	0	-7.250846	1.880045	0.006120
8	16	0	-5.951027	2.855479	0.006952
9	7	0	-4.748895	1.763407	0.003973
10	6	0	-0.595616	-0.755588	-0.003714
11	6	0	0.123569	-1.963520	-0.006522
12	6	0	1.506081	-1.952284	-0.007417
13	6	0	2.237455	-0.749525	-0.005701
14	6	0	1.505289	0.454599	-0.002535
15	6	0	0.124885	0.455587	-0.001701
16	6	0	-2.008680	-0.746789	-0.002672
17	6	0	3.689483	-0.813680	-0.007055
18	6	0	-3.226531	-0.718547	-0.001720
19	6	0	4.542326	0.233780	-0.010744
20	6	0	5.992951	0.190881	-0.011871
21	6	0	6.717388	1.393239	-0.022443
22	6	0	8.100332	1.426733	-0.023931
23	6	0	8.850483	0.231927	-0.018295
24	6	0	8.128233	-0.983876	-0.001412
25	6	0	6.747353	-0.995131	0.000047
26	7	0	10.222759	0.246389	-0.029965

27	6	0	10.958103	-0.992439	0.050789
28	6	0	10.927544	1.504043	0.025393
29	7	0	-8.960155	-0.648415	0.002847
30	8	0	-9.565443	0.408465	0.005249
31	8	0	-9.483206	-1.756369	0.001215
32	1	0	-7.391033	-2.701913	-0.002164
33	1	0	-4.914527	-2.801628	-0.004276
34	1	0	-0.417949	-2.904669	-0.007989
35	1	0	2.046989	-2.895690	-0.009697
36	1	0	2.027398	1.406633	-0.000263
37	1	0	-0.423614	1.392665	0.000783
38	1	0	4.097182	-1.823689	-0.005748
39	1	0	4.126842	1.241439	-0.014317
40	1	0	6.172861	2.335452	-0.027930
41	1	0	8.600313	2.388577	-0.028670
42	1	0	8.655891	-1.930897	0.012002
43	1	0	6.242874	-1.957468	0.013482
44	1	0	10.748839	-1.540707	0.981156
45	1	0	10.726017	-1.654784	-0.793915
46	1	0	12.027459	-0.777757	0.019332
47	1	0	10.678271	2.143054	-0.832354
48	1	0	10.703772	2.065586	0.944451
49	1	0	12.001957	1.315724	-0.002103

Ground to excited state transition electric dipole moments (Au):

state	X	Y	Z	Dip. S.	Osc.
1	3.8246	0.0061	0.0008	14.6277	0.6837
2	-3.1095	0.0685	0.0009	9.6739	0.6762
3	-3.1168	-0.3284	-0.0079	9.8222	0.7674
4	0.0000	-0.0000	0.0084	0.0001	0.0000
5	-0.8589	-0.0611	-0.0059	0.7416	0.0633
6	0.2221	-0.0175	-0.0019	0.0496	0.0045
7	0.0001	-0.0002	0.0111	0.0001	0.0000
8	0.0905	-0.1514	-0.0003	0.0311	0.0029
9	0.0077	0.0134	-0.0001	0.0002	0.0000
10	-0.0000	0.0002	-0.0448	0.0020	0.0002
11	1.0201	-0.5727	-0.0046	1.3686	0.1373
12	-0.5421	-0.4678	-0.0040	0.5127	0.0520
13	-0.9117	-0.9460	0.0037	1.7263	0.1779
14	0.2356	-0.0407	0.0043	0.0572	0.0060
15	0.0002	0.0000	0.0149	0.0002	0.0000
16	0.3311	0.2348	0.0021	0.1647	0.0177
17	0.0638	-0.2314	0.0018	0.0576	0.0063
18	0.4259	0.0379	0.0138	0.1830	0.0205
19	-0.1467	0.3115	-0.0029	0.1185	0.0140
20	0.2609	0.4353	0.0112	0.2577	0.0307
21	-0.0000	-0.0000	0.0115	0.0001	0.0000
22	0.0112	-0.0984	-0.0034	0.0098	0.0012
23	0.2321	0.2660	0.0037	0.1246	0.0153
24	0.4151	0.5762	0.0018	0.5044	0.0628
25	-0.0001	-0.0000	0.0308	0.0009	0.0001
26	0.3501	0.1603	0.0018	0.1483	0.0189
27	-0.0001	0.0002	-0.0204	0.0004	0.0001
28	-0.0759	-0.0891	0.0048	0.0137	0.0018
29	-0.0000	0.0001	-0.0101	0.0001	0.0000

30	0.6091	0.1798	0.0065	0.4033	0.0527
31	0.3766	-0.1863	0.1628	0.2030	0.0271
32	0.0010	-0.4933	-0.1686	0.2718	0.0364
33	-0.1847	-0.1904	0.3281	0.1780	0.0239
34	0.0014	-0.5091	-0.0117	0.2593	0.0351
35	0.0008	-0.0039	-0.0113	0.0001	0.0000
36	-0.1515	-0.3911	-0.0002	0.1759	0.0240
37	0.2428	0.4470	-0.0044	0.2588	0.0353
38	-0.0002	-0.0003	-0.0263	0.0007	0.0001
39	-0.0728	-0.2669	0.0004	0.0765	0.0106
40	-0.0001	0.0002	-0.0692	0.0048	0.0007

Standard basis: TZVP (5D, 7F)

SCF Done:E(RPBE1PBE) = -1691.62704981 a.u.

Table 11. BTN-3 Optimization of Ground State Geometry in Chloroform Solvent and Mulliken charges

Standard orientation:

Center	Atomic	Atomic	Coordinates	(Angstroms)	
Number	Number	Type	X	Y	Z
1	6	0	-6.826228	-1.792691	0.001813
2	6	0	-7.528823	-0.606668	0.001769
3	6	0	-6.809099	0.631810	0.001082
4	6	0	-5.352518	0.576162	0.000454
5	6	0	-4.642146	-0.680208	0.000511
6	6	0	-5.416111	-1.836424	0.001203
7	7	0	-7.288065	1.879327	0.000913
8	16	0	-5.984090	2.877956	0.000106
9	7	0	-4.768430	1.775080	-0.000173
10	6	0	-0.599990	-0.749746	0.003908
11	6	0	0.122725	-1.961388	-0.001561
12	6	0	1.508270	-1.951586	-0.002205
13	6	0	2.244299	-0.746155	-0.002587
14	6	0	1.509406	0.461860	0.002886
15	6	0	0.125914	0.464024	0.008707
16	6	0	-2.015150	-0.740578	0.004543
17	6	0	3.700029	-0.811689	-0.003243
18	6	0	-3.234280	-0.711415	0.005084
19	6	0	4.559327	0.235235	0.001698
20	6	0	6.013870	0.190490	-0.009363
21	6	0	6.742371	1.395687	-0.014706
22	6	0	8.128650	1.427789	-0.030922
23	6	0	8.881127	0.229255	-0.057455
24	6	0	8.154736	-0.989295	-0.031292
25	6	0	6.770432	-0.999522	-0.015076
26	7	0	10.260837	0.242889	-0.110116
27	6	0	11.003914	-1.005373	0.076922
28	6	0	10.975242	1.507658	0.072047
29	7	0	-8.988964	-0.666970	0.002421
30	8	0	-9.610336	0.392477	0.002239
31	8	0	-9.511804	-1.787062	0.003027
32	1	0	-7.395251	-2.714501	0.002348
33	1	0	-4.920399	-2.800959	0.001273
34	1	0	-0.418473	-2.902605	-0.006475
35	1	0	2.047405	-2.895790	-0.007611
36	1	0	2.032029	1.413265	0.007779
37	1	0	-0.420247	1.402246	0.008894

38	1	0	4.104908	-1.822432	-0.019125
39	1	0	4.146840	1.243650	0.012417
40	1	0	6.199442	2.338591	0.001289
41	1	0	8.628313	2.389081	-0.025783
42	1	0	8.680424	-1.936753	-0.026453
43	1	0	6.265442	-1.961333	0.000615
44	1	0	10.835931	-1.472526	1.080474
45	1	0	10.731068	-1.753542	-0.697458
46	1	0	12.072748	-0.786454	-0.032839
47	1	0	10.682335	2.245530	-0.707304
48	1	0	10.797698	1.974433	1.070534
49	1	0	12.048901	1.313798	-0.043029

Mulliken charges:

1	C	-0.202067	26	N	-0.513617
2	C	0.288780	27	C	-0.386916
3	C	0.221858	28	C	-0.387078
4	C	0.243188	29	N	0.359572
5	C	-0.001247	30	O	-0.400317
6	C	-0.187330	31	O	-0.422065
7	N	-0.560971	32	H	0.242945
8	S	0.646168	33	H	0.221700
9	N	-0.584240	34	H	0.199552
10	C	-0.026616	35	H	0.191056
11	C	-0.160873	36	H	0.192636
12	C	-0.238448	37	H	0.204237
13	C	0.137748	38	H	0.177679
14	C	-0.224731	39	H	0.180336
15	C	-0.156200	40	H	0.182075
16	C	-0.062766	41	H	0.183934
17	C	-0.239189	42	H	0.184295
18	C	0.022478	43	H	0.183285
19	C	-0.211253	44	H	0.186770
20	C	0.112691	45	H	0.197528
21	C	-0.241250	46	H	0.198867
22	C	-0.240019	47	H	0.196872
23	C	0.367148	48	H	0.187754
24	C	-0.238626	49	H	0.198588
25	C	-0.223919			

Standard basis: 6-31G(d) (6D, 7F)

SCF Done: E(RPBE1PBE) = -1691.23547732 a.u.

Table 12. BTN-3 Calculation of excited state geometry in chloroform solvent

Standard orientation:

Center	Atomic	Atomic	Coordinates (Angstroms)		
Number	Number	Type	X	Y	Z
1	6	0	-6.826228	-1.792691	0.001813
2	6	0	-7.528823	-0.606668	0.001769
3	6	0	-6.809099	0.631810	0.001082

4	6	0	-5.352518	0.576162	0.000454
5	6	0	-4.642146	-0.680208	0.000511
6	6	0	-5.416111	-1.836424	0.001203
7	7	0	-7.288065	1.879327	0.000913
8	16	0	-5.984090	2.877956	0.000106
9	7	0	-4.768430	1.775080	-0.000173
10	6	0	-0.599990	-0.749746	0.003908
11	6	0	0.122725	-1.961388	-0.001561
12	6	0	1.508270	-1.951586	-0.002205
13	6	0	2.244299	-0.746155	-0.002587
14	6	0	1.509406	0.461860	0.002886
15	6	0	0.125914	0.464024	0.008707
16	6	0	-2.015150	-0.740578	0.004543
17	6	0	3.700029	-0.811689	-0.003243
18	6	0	-3.234280	-0.711415	0.005084
19	6	0	4.559327	0.235235	0.001698
20	6	0	6.013870	0.190490	-0.009363
21	6	0	6.742371	1.395687	-0.014706
22	6	0	8.128650	1.427789	-0.030922
23	6	0	8.881127	0.229255	-0.057455
24	6	0	8.154736	-0.989295	-0.031292
25	6	0	6.770432	-0.999522	-0.015076
26	7	0	10.260837	0.242889	-0.110116
27	6	0	11.003914	-1.005373	0.076922
28	6	0	10.975242	1.507658	0.072047
29	7	0	-8.988964	-0.666970	0.002421
30	8	0	-9.610336	0.392477	0.002239
31	8	0	-9.511804	-1.787062	0.003027
32	1	0	-7.395251	-2.714501	0.002348
33	1	0	-4.920399	-2.800959	0.001273
34	1	0	-0.418473	-2.902605	-0.006475
35	1	0	2.047405	-2.895790	-0.007611
36	1	0	2.032029	1.413265	0.007779
37	1	0	-0.420247	1.402246	0.008894
38	1	0	4.104908	-1.822432	-0.019125
39	1	0	4.146840	1.243650	0.012417
40	1	0	6.199442	2.338591	0.001289
41	1	0	8.628313	2.389081	-0.025783
42	1	0	8.680424	-1.936753	-0.026453
43	1	0	6.265442	-1.961333	0.000615
44	1	0	10.835931	-1.472526	1.080474
45	1	0	10.731068	-1.753542	-0.697458
46	1	0	12.072748	-0.786454	-0.032839
47	1	0	10.682335	2.245530	-0.707304
48	1	0	10.797698	1.974433	1.070534
49	1	0	12.048901	1.313798	-0.043029

Ground to excited state transition electric dipole moments (Au):

state	X	Y	Z	Dip. S.	Osc.
1	4.4531	0.0338	0.0007	19.8312	0.8092
2	-3.3776	0.0641	0.0017	11.4121	0.7491
3	-2.9193	-0.3998	-0.0074	8.6821	0.6390
4	1.4281	0.1456	0.0071	2.0607	0.1604
5	0.5871	-0.0099	-0.0006	0.3448	0.0301
6	-0.0001	0.0001	-0.0072	0.0001	0.0000
7	-0.0453	0.1441	0.0001	0.0228	0.0021

8	0.0472	-0.1287	-0.0004	0.0188	0.0017
9	0.0000	0.0004	0.0060	0.0000	0.0000
10	0.6528	-0.9736	-0.0061	1.3740	0.1342
11	1.1711	0.6868	0.0001	1.8431	0.1814
12	-0.0466	-0.6821	0.0055	0.4674	0.0469
13	0.0000	-0.0001	0.0486	0.0024	0.0002
14	0.0234	-0.2770	0.0067	0.0773	0.0080
15	-0.9457	-0.5245	0.0021	1.1695	0.1217
16	0.0760	-0.0897	0.0033	0.0138	0.0015
17	0.5208	0.1365	0.0130	0.2901	0.0315
18	-0.0001	-0.0001	0.0210	0.0004	0.0000
19	-0.2927	-0.4001	-0.0094	0.2458	0.0285
20	-0.2287	-0.0492	-0.0021	0.0547	0.0065
21	-0.1663	-0.4254	-0.0033	0.2086	0.0254
22	0.2718	0.4980	-0.0024	0.3218	0.0393
23	-0.3081	-0.4536	0.0020	0.3007	0.0370
24	-0.1801	0.0944	0.0028	0.0414	0.0051
25	-0.0000	-0.0002	0.0349	0.0012	0.0002
26	-0.0474	0.1141	-0.0029	0.0153	0.0019
27	0.0000	0.0001	-0.0094	0.0001	0.0000
28	0.4619	-0.2827	0.0030	0.2933	0.0377
29	-0.0009	0.0017	0.0186	0.0003	0.0000
30	0.0874	0.1519	-0.0032	0.0307	0.0040
31	0.3153	-0.5816	0.0221	0.4381	0.0569
32	0.2182	0.2882	0.0145	0.1309	0.0171
33	0.5936	0.7208	0.0233	0.8725	0.1144
34	0.0000	0.0001	-0.0376	0.0014	0.0002
35	0.0000	-0.0002	0.0000	0.0000	0.0000
36	-0.0010	-0.0098	-0.0035	0.0001	0.0000
37	0.0929	0.7554	-0.0030	0.5792	0.0790
38	-0.1201	-0.2483	0.0129	0.0762	0.0104
39	-0.0034	-0.0012	0.0049	0.0000	0.0000
40	0.1363	0.8996	-0.0056	0.8280	0.1148

Standard basis: TZVP (5D, 7F)

SCF Done: E(RPBE1PBE) = -1691.64118186 a.u.