Supporting Information

Protonation induced shifting of electron-accepting center in intramolecular charge transfer chromophores and theoretical study†

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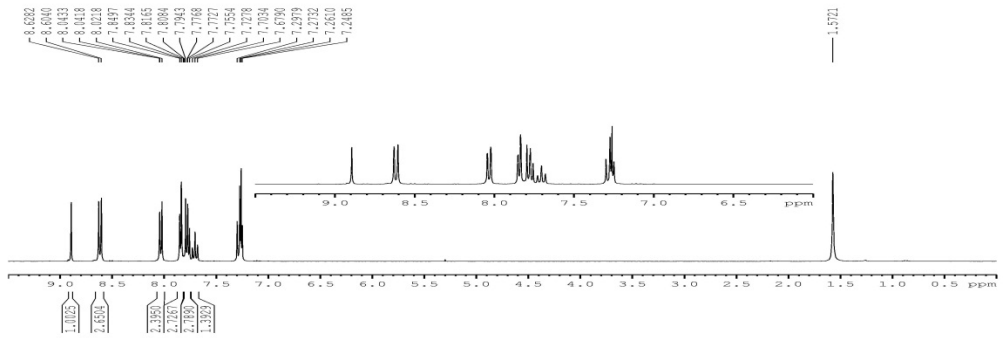
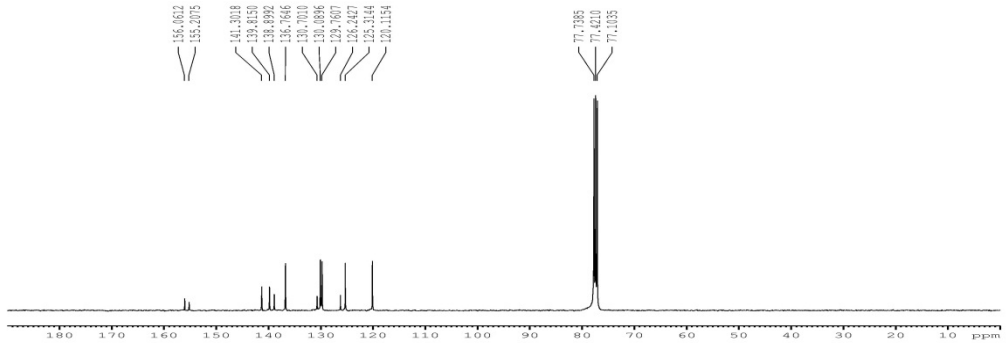
Supporting Characterizations

Instrumentation. ^{1}H-NMR (400.13 MHZ) and ^{13}C-NMR (100.61 MHZ) spectra were recorded on Bruker DRX 400-MHZ NMR spectrometer in the solvent of $CDCl_3$ at room temperature. Tetramethylsilane (TMS) was used as an internal standard to express chemical shift. Mass spectra were measured on a Bruker micrOTOFQII. UV-vis-NIR spectra were conducted on Agilent Cary 5000. Electrochemistry was performed with distilled solvents and recrystallized electrolytes using a three-electrode cell with a platinum flag as the counter electrode, a silver wire pseudo-reference electrode calibrated using a 5 mM solution of Fc/Fc^{+} in 0.1 M electrolyte solution, and a an ITO-coated glass slide (7 × 40 × 0.7 mm, 20 Ω cm^{-1}, Delta Technologies, Ltd) as the working electrode. Cyclic voltammetry (CV) measurements were conducted on Autolab PGSTAT 30 electrochemical workstation.

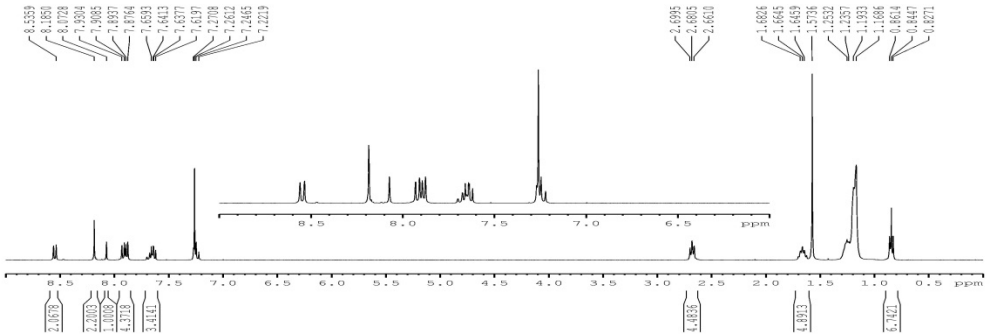
(a)



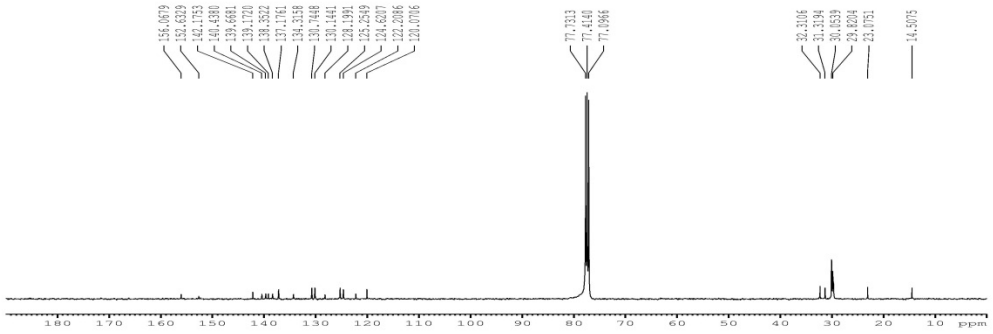
(b)



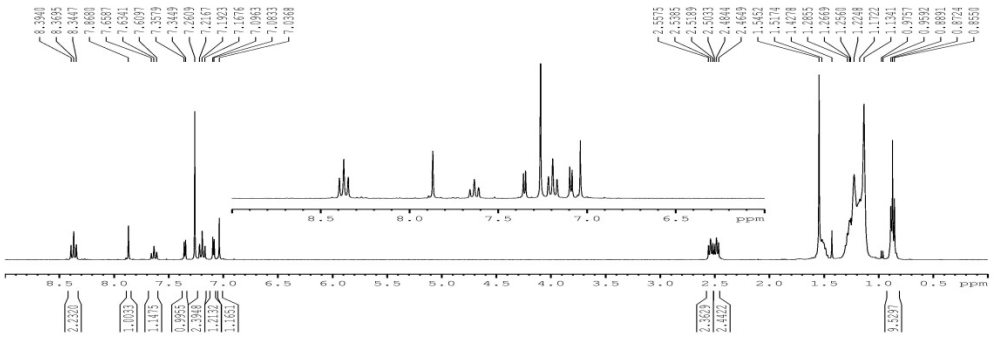
(c)



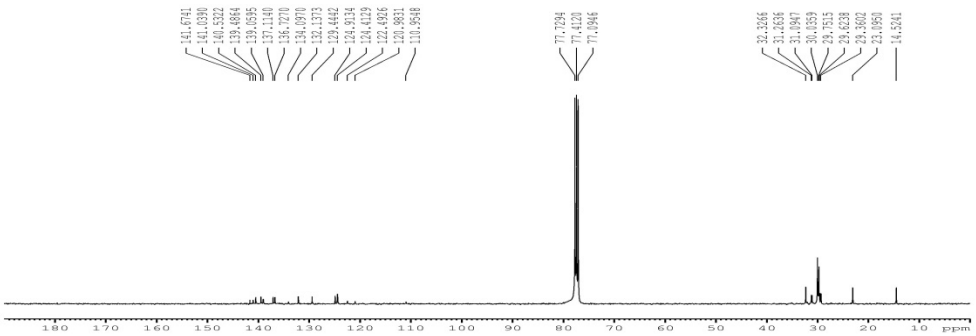
(d)



(e)



(f)



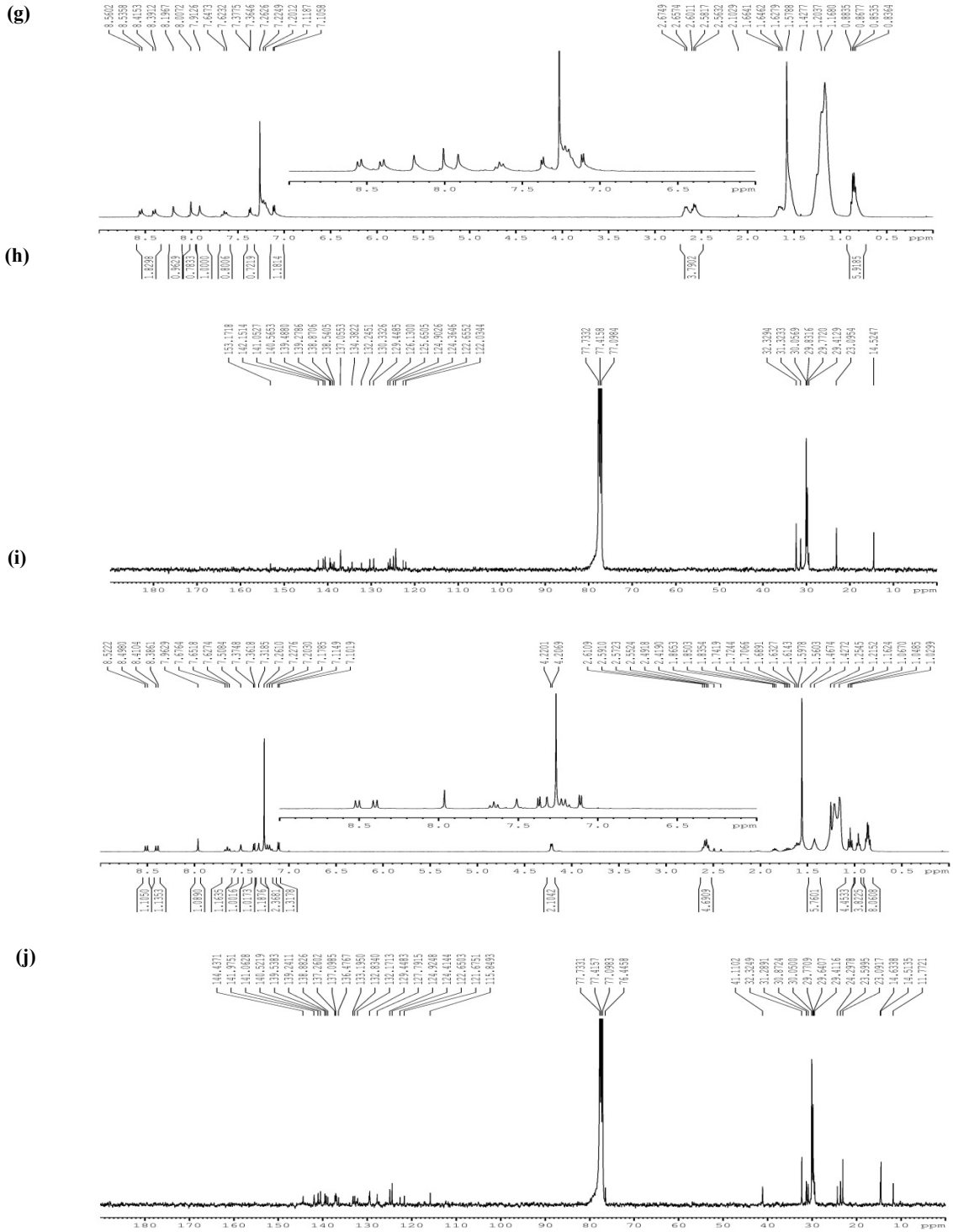


Fig. S1 NMR spectra of monomers and polymer. (a) and (b), ^{1}H-NMR and ^{13}C-NMR spectra of monomer **BTAz-1**; (c) and (d), ^{1}H-NMR and ^{13}C-NMR spectra of monomer **BTAz-2**; (e) and (f), ^{1}H-NMR and ^{13}C-NMR spectra of monomer 5-bromo-3-dodecyl-2-(3-(3-dodecylthiophen-2-yl)azulen-1-yl)thiophene **5**; (g) and (h), ^{1}H-NMR and ^{13}C-NMR spectra of monomer **BTAz-3**; (i) and (j), ^{1}H-NMR and ^{13}C-NMR spectra of monomer **BTAz-4**.

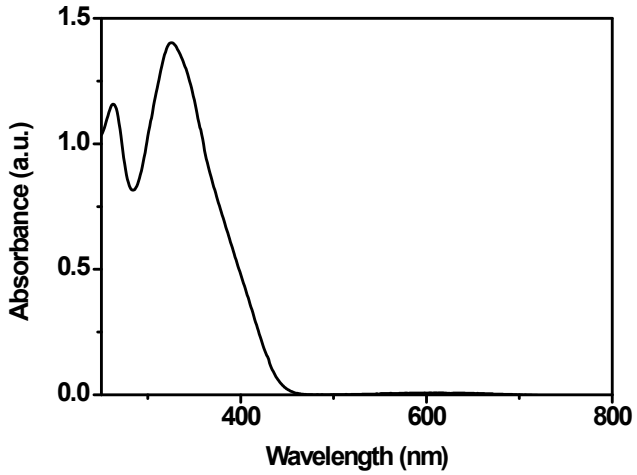
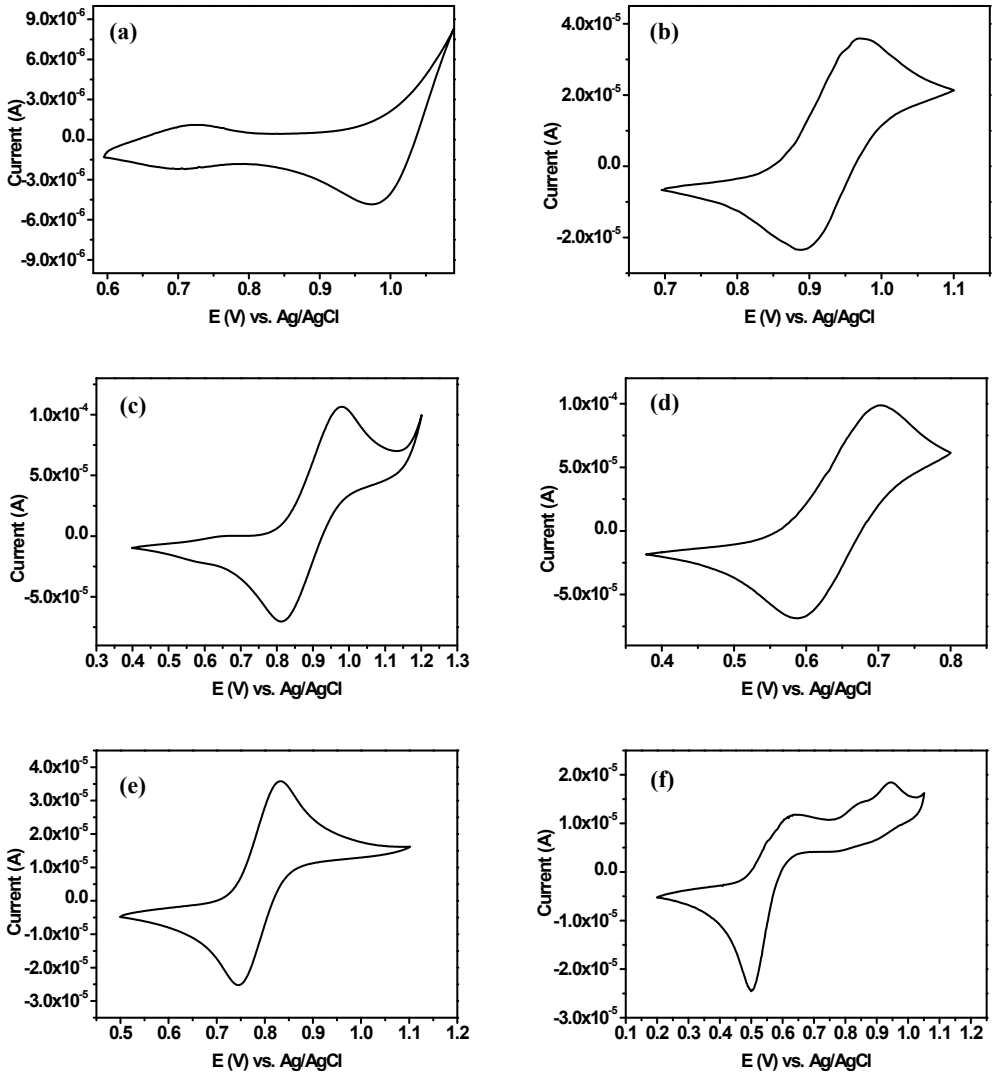


Fig. S2 UV-vis spectrum of **BTATB** in chloroform.



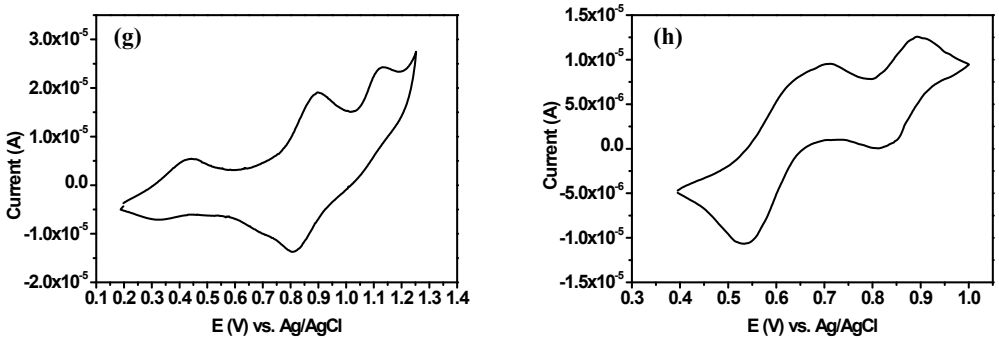


Fig. S3 Cyclic voltammograms of **BTAz-1** (a and b), **BTAz-2** (c and d), **BTAz-3** (e and f) and **BTAz-4** (g and h) in dichloromethane (a, c, e and g) and dichloromethane/TFA (v/v:8.5/1.5; b, d, f and h). CV experiments (a-h) performed with 0.1 mM oligomer and 0.1 M tetrabutylammonium perchlorate (scan rate 25 mV/s).

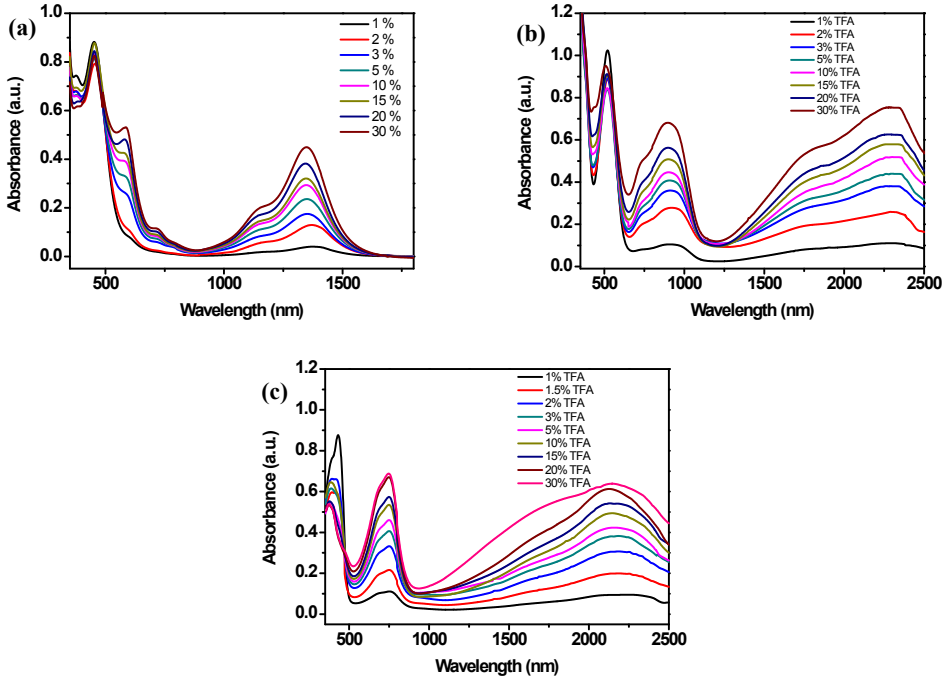
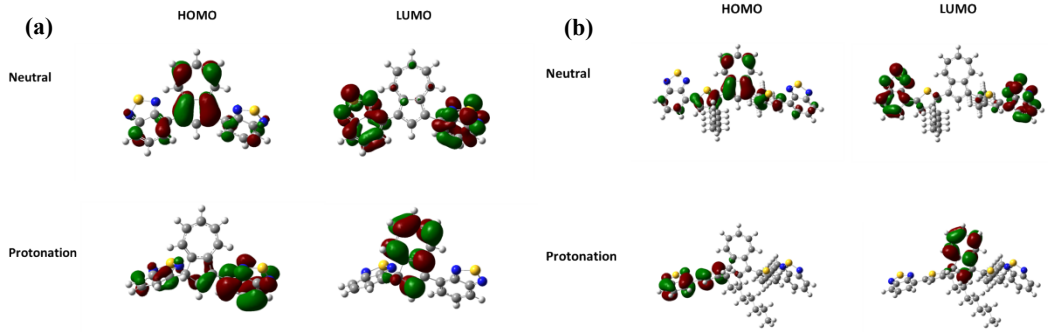


Fig. S4 UV-vis-NIR spectrum of **BTAz**s under different TFA concentration in chloroform solution: (a): **BTAz-2**; (b) **BTAz-3**; (c) **BTAz-4**.



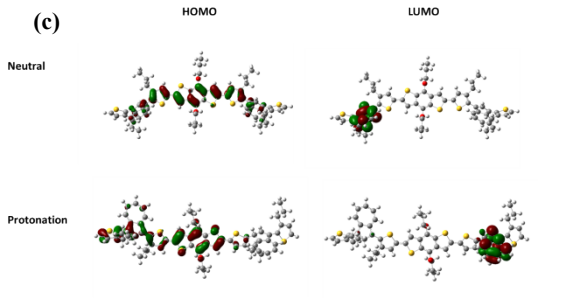


Fig. S5 Spatial distributions of the calculated HOMOs and LUMOs of model compounds **BTAz-1** (a), **BTAz-2** (b), and **BTAz-4** (c) at different degree of protonation: neutral and protonation.

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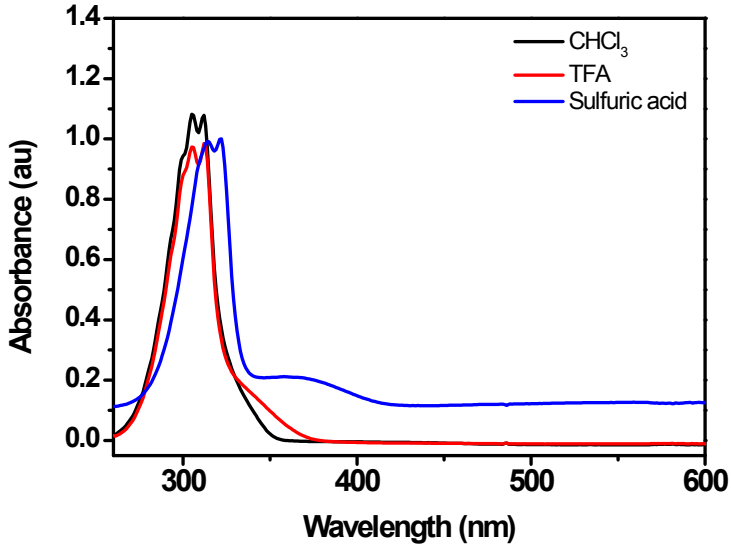

Fig. S6 UV-Vis spectra of 2,1,3-benzothiadiazole in chloroform (dark line); chloroform/TFA (v/v: 7/3, red line) and chloroform/sulfuric acid (v/v: 7/3, blue line).

Cartesian coordinates of the DFT optimized ground-state

Cartesian coordinates of the DFT optimized ground-state of BTAz-1

C	-2.44847	-0.87882	0.605565	C	4.941283	-1.10619	-0.3267
C	-1.20419	3.510492	0.37495	C	3.681084	-0.46385	0.018284
C	0.000007	4.109789	0.000001	C	-2.55622	-1.91411	1.517202
C	1.204204	3.510485	-0.37495	C	-3.79356	-2.54112	1.852378
C	1.522541	2.151277	-0.43728	C	-4.98093	-2.1572	1.285319
C	0.725357	1.040488	-0.1704	C	-4.94129	-1.10617	0.326703
C	-0.72535	1.040493	0.1704	C	-3.68109	-0.46385	-0.01829
C	-1.52253	2.151282	0.437281	N	-3.81057	0.481142	-0.95747
C	-1.13386	-0.31876	0.256345	S	-5.40715	0.542306	-1.34591

C	-4E-06	-1.11043	0.000003	N	-5.9937	-0.62536	-0.34752
C	1.133859	-0.31877	-0.25634	N	3.810576	0.481153	0.957454
H	-2.0107	4.191694	0.636388	S	5.407152	0.542324	1.345875
H	0.000011	5.198651	0.000001	N	5.9937	-0.62535	0.347502
H	2.010712	4.191686	-0.63639	H	1.654711	-2.25642	-2.01712
H	2.545022	1.930113	-0.72758	H	3.781227	-3.34119	-2.58759
C	-2.54501	1.930122	0.727579	H	5.927351	-2.62455	-1.53413
C	2.44846	-0.87883	-0.60556	H	-1.65473	-2.25639	2.017155
C	2.556213	-1.91414	-1.51718	H	-3.78125	-3.34114	2.587634
C	3.793549	-2.54116	-1.85234	H	-5.92736	-2.62451	1.534155
C	4.980921	-2.15723	-1.2853	H	-5E-06	-2.19544	0.000004

Cartesian coordinates of the DFT optimized ground-state of BTAz-2

C	-6.35522	0.348308	-0.58816	S	3.799919	-0.70561	0.590867
C	-4.96206	-0.07338	-0.46508	H	4.873597	1.739366	-1.85009
C	-4.34201	-1.0948	-1.15719	C	2.140733	2.383061	-1.48266
C	-2.96004	-1.26959	-0.87241	C	2.57201	3.785768	-1.00839
C	-2.50599	-0.35743	0.067449	C	1.760531	4.913025	-1.65885
S	-3.79992	0.70561	0.590867	C	2.181531	6.313217	-1.19391
H	-4.8736	-1.73936	-1.8501	H	2.22174	2.338403	-2.57856
C	-2.14073	-2.38306	-1.48267	H	1.082103	2.239044	-1.24468
C	-2.57201	-3.78577	-1.00839	H	3.63984	3.933508	-1.2227
C	-1.76053	-4.91302	-1.65885	H	2.470741	3.838287	0.084175
C	-2.18153	-6.31322	-1.19391	H	0.692401	4.763832	-1.44296
H	-2.22174	-2.3384	-2.57856	H	1.860837	4.848044	-2.75283
H	-1.0821	-2.23904	-1.24469	H	3.252512	6.457367	-1.40075
H	-3.63984	-3.93351	-1.22269	H	2.072402	6.380709	-0.10138
H	-2.47073	-3.83828	0.084174	C	1.382404	7.444423	-1.85403
H	-0.6924	-4.76383	-1.44297	C	1.80455	8.844521	-1.39058
H	-1.86084	-4.84804	-2.75283	C	1.012082	9.977121	-2.05606
H	-3.25251	-6.45737	-1.40074	C	1.4409	11.37153	-1.58784
H	-2.07239	-6.38071	-0.10138	H	1.491828	7.375709	-2.94677
C	-1.3824	-7.44442	-1.85404	H	0.311419	7.301166	-1.64745
C	-1.80455	-8.84452	-1.39058	H	2.876946	8.986352	-1.59241
C	-1.01208	-9.97712	-2.05607	H	1.690405	8.916072	-0.29849
C	-1.4409	-11.3715	-1.58784	H	-0.0593	9.836656	-1.85385
H	-1.49184	-7.37571	-2.94677	H	1.126566	9.905984	-3.14719
H	-0.31142	-7.30116	-1.64747	H	0.858363	12.15743	-2.08219
H	-2.87694	-8.98635	-1.5924	H	2.500273	11.55467	-1.80635
H	-1.69039	-8.91607	-0.29849	H	1.303047	11.48583	-0.50548
H	0.059303	-9.83665	-1.85387	C	6.355217	-0.34831	-0.58816
H	-1.12658	-9.90598	-3.1472	C	7.145805	0.055451	-1.65369
H	-0.85836	-12.1574	-2.08219	C	8.515399	-0.30738	-1.79494
H	-2.50027	-11.5547	-1.80634	C	9.160123	-1.10938	-0.88752
H	-1.30303	-11.4858	-0.50548	C	8.402783	-1.57747	0.221014
C	-1.23389	-0.2674	4.416549	C	7.00578	-1.2021	0.375432
C	-1E-06	-2E-06	5.014197	C	-7.14581	-0.05545	-1.65369

C	1.233888	0.267393	4.416549	C	-8.5154	0.307375	-1.79494
C	1.556331	0.305171	3.056371	C	-9.16012	1.10938	-0.88752
C	0.736365	0.115421	1.947022	C	-8.40278	1.577466	0.221015
C	-0.73637	-0.11542	1.947022	C	-7.00578	1.202099	0.375431
C	-1.55633	-0.30517	3.056371	N	-6.43621	1.725183	1.464617
C	-1.15044	-0.1692	0.58698	S	-7.59137	2.620235	2.219816
C	0	0	-0.20766	N	-8.85465	2.374801	1.197423
C	1.150437	0.169198	0.586981	N	6.436208	-1.72518	1.464617
H	-2.05935	-0.45865	5.098262	S	7.591369	-2.62024	2.219816
H	-1E-06	-2E-06	6.10312	N	8.854647	-2.3748	1.197422
H	2.059343	0.45865	5.098263	H	6.704471	0.668841	-2.43228
H	2.600396	0.511757	2.831513	H	9.054003	0.06401	-2.66248
H	-2.6004	-0.51176	2.831512	H	10.20059	-1.39548	-0.99264
C	4.962064	0.073382	-0.46508	H	-6.70447	-0.66884	-2.43228
C	4.342013	1.094806	-1.15719	H	-9.05401	-0.06401	-2.66248
C	2.960042	1.269592	-0.8724	H	-10.2006	1.395479	-0.99264
C	2.505991	0.357433	0.06745	H	0	0.000001	-1.29169

Cartesian coordinates of the DFT optimized ground-state of BTAz-3

N	1.243697	-1.25958	-0.15913	H	8.906459	-1.35218	5.620416
C	0.722784	-0.03157	-0.09291	C	-2.91419	1.240454	0.385147
C	-0.72279	-0.03157	0.092826	C	-3.68287	2.362089	0.635709
N	-1.24371	-1.25958	0.158999	C	-5.07762	2.126613	0.767926
S	-1.1E-05	-2.32099	-8.9E-05	C	-5.39376	0.785182	0.617169
C	-1.47092	1.193302	0.189632	S	-3.95481	-0.17058	0.30825
C	-0.7009	2.345665	0.08528	H	-3.25686	3.35422	0.745045
C	0.700913	2.345663	-0.08527	C	-6.05393	3.22452	1.120225
C	1.470921	1.193299	-0.18967	C	-5.8993	3.731116	2.568803
H	-1.19092	3.312466	0.133904	C	-6.87609	4.861471	2.905927
H	1.19094	3.312462	-0.13384	H	-5.91785	4.071128	0.431695
C	2.914194	1.24045	-0.38518	H	-7.08053	2.871957	0.978781
C	3.682871	2.362083	-0.63575	H	-4.86783	4.072971	2.728471
C	5.077621	2.126608	-0.76795	H	-6.05127	2.888553	3.255676
C	5.393766	0.785178	-0.61718	H	-7.91656	4.535059	2.788076
S	3.954806	-0.17058	-0.30827	H	-6.72472	5.726981	2.248781
H	3.25686	3.354212	-0.7451	C	-6.70401	-2.71262	3.185269
C	6.053931	3.224512	-1.12025	C	-7.89612	-3.44025	3.218975
C	5.89932	3.731095	-2.56883	C	-9.06834	-3.25663	2.481519
C	6.876116	4.861448	-2.90596	C	-9.35625	-2.272	1.531307
H	5.917846	4.071126	-0.43173	C	-8.55103	-1.24075	1.055732
H	7.080533	2.871953	-0.97879	C	-7.13064	-0.96434	1.416783
H	4.86785	4.072947	-2.72851	C	-6.36698	-1.62185	2.377496
H	6.051304	2.888526	-3.2557	C	-6.70997	0.145304	0.633086
H	7.916586	4.535038	-2.78809	C	-7.81034	0.542443	-0.15366
H	6.72474	5.726964	-2.24882	C	-8.93044	-0.27478	0.08541
C	6.704045	-2.71263	-3.18526	H	-5.92759	-3.044	3.870934
C	7.896155	-3.44026	-3.21895	H	-7.91446	-4.27086	3.922974

C	9.068363	-3.25663	-2.48148	H	-9.86889	-3.96569	2.679562
C	9.356264	-2.27201	-1.53127	H	-10.354	-2.31493	1.098841
C	8.551039	-1.24075	-1.0557	H	-5.36172	-1.23068	2.518578
C	7.130656	-0.96434	-1.41677	C	-12.6685	0.291719	-1.0256
C	6.367001	-1.62186	-2.37749	C	-11.9343	0.097647	-2.1595
C	6.709974	0.145301	-0.63308	C	-10.5415	-0.14447	-1.91611
C	7.810334	0.542444	0.153678	C	-10.235	-0.13069	-0.56938
C	8.930437	-0.27478	-0.08538	S	-11.6768	0.192991	0.391152
H	5.927634	-3.04402	-3.87093	H	-12.3644	0.120673	-3.15625
H	7.914506	-4.27088	-3.92294	C	-9.56285	-0.44577	-3.02644
H	9.868923	-3.9657	-2.67951	C	-9.79484	-1.82198	-3.68233
H	10.35399	-2.31493	-1.09879	C	-8.81527	-2.10311	-4.82567
H	5.361739	-1.23069	-2.51858	C	-9.63623	0.332476	-3.80015
C	12.66847	0.291727	1.025661	H	-8.53859	-0.40497	-2.64126
C	11.93423	0.097656	2.15956	H	-10.8261	-1.87942	-4.05573
C	10.54149	-0.14447	1.916153	H	-9.7047	-2.59982	-2.91305
C	10.23498	-0.13069	0.569418	H	-7.77723	-2.08544	-4.47185
S	11.6768	0.192995	-0.3911	H	-8.90652	-1.35218	-5.62039
H	12.36437	0.120685	3.156311	H	7.794705	1.366573	0.858121
C	9.562822	-0.44576	3.026475	H	13.72937	0.485803	0.938827
C	9.794804	-1.82197	3.682365	H	-7.79472	1.36657	-0.85811
C	8.815226	-2.1031	4.825702	H	-13.7294	0.485793	-0.93875
H	9.636192	0.332484	3.80018	H	8.997869	-3.08645	5.273776
H	8.538565	-0.40497	2.641288	H	6.74888	5.20184	-3.93986
H	10.82606	-1.87941	4.055784	H	-6.74884	5.201872	3.939831
H	9.704674	-2.59981	2.913084	H	-8.99792	-3.08646	-5.27374
H	7.777181	-2.08544	4.47187				

Cartesian coordinates of the DFT optimized ground-state of BTAz-4

C	1.305033	0.599774	-0.17844	S	-13.597	-0.70087	0.296129
C	1.129074	1.995461	0.046158	H	-14.0155	-2.10597	-3.00693
C	-0.12511	2.583746	0.161712	C	-11.1928	-2.29214	-2.57606
C	-1.25713	1.750522	0.073782	C	-11.2907	-3.82114	-2.75056
C	-1.08072	0.355773	-0.15598	C	-10.2009	-4.38025	-3.66989
C	0.173688	-0.22893	-0.29544	H	-11.248	-1.81863	-3.56744
C	2.688698	0.236423	-0.23679	H	-10.2067	-2.04472	-2.16939
C	3.548166	1.290773	-0.07361	H	-12.2803	-4.08158	-3.14945
S	2.675639	2.821588	0.171562	H	-11.2252	-4.29506	-1.76258
S	-2.62437	-0.4804	-0.21688	H	-9.20039	-4.16481	-3.27538
C	-3.49453	1.038068	0.08585	H	-10.2624	-3.94032	-4.67313
C	-2.63884	2.100267	0.215736	C	4.994161	1.280606	-0.06731
O	-0.25121	3.932378	0.406924	C	5.86434	2.314516	0.198081
O	0.30198	-1.58493	-0.49026	C	7.246797	1.973089	0.115152
H	3.021311	-0.78711	-0.36789	C	7.441912	0.645737	-0.22331
H	-2.97202	3.10264	0.45709	S	5.897506	-0.17748	-0.4284
C	0.402318	-1.99283	-1.86936	H	5.522689	3.313284	0.453339
C	0.518058	-3.50913	-1.90335	C	8.34453	2.991087	0.315481

C	0.637242	-4.04928	-3.33215	C	8.410558	4.045078	-0.8087
H	-0.48797	-1.65355	-2.41721	C	9.513803	5.081681	-0.57741
H	1.282267	-1.51976	-2.32826	H	8.193941	3.505451	1.275706
H	-0.36074	-3.93758	-1.40632	H	9.313222	2.485721	0.382875
H	1.524043	-3.65001	-3.8393	H	7.439475	4.550666	-0.89462
H	-0.23926	-3.78384	-3.93549	H	8.57394	3.53231	-1.76544
C	-0.43221	4.748307	-0.76708	H	10.50004	4.605044	-0.52126
C	-0.53401	6.198407	-0.31893	H	9.355999	5.627148	0.361331
C	-0.72868	7.158449	-1.49676	C	8.829583	-1.78699	-3.78322
H	0.418737	4.605836	-1.44792	C	9.946088	-2.60714	-3.96438
H	-1.34336	4.433887	-1.29606	C	11.004	-2.8703	-3.09093
H	-1.36833	6.288535	0.387931	C	11.23	-2.35219	-1.81179
H	0.109589	7.103222	-2.20177	C	10.45454	-1.46806	-1.06686
H	-0.80052	8.193921	-1.14793	C	9.131969	-0.89114	-1.44403
C	-4.94169	1.061095	0.16675	C	8.468689	-1.03684	-2.65961
C	-5.78157	2.1299	-0.05487	C	8.691833	-0.10596	-0.34388
C	-7.16721	1.85126	0.135632	C	9.691252	-0.17594	0.647503
C	-7.39534	0.535483	0.501259	C	10.76466	-0.98648	0.233638
S	-5.87804	-0.34991	0.611218	H	8.141402	-1.73187	-4.62358
H	-5.41279	3.101578	-0.36807	H	9.999681	-3.11426	-4.92655
C	-8.23388	2.911663	-0.00622	H	11.7608	-3.55995	-3.45762
C	-8.13509	4.022967	1.058362	H	12.14403	-2.6871	-1.32554
C	-9.21053	5.099519	0.885755	H	7.53411	-0.48649	-2.74649
H	-8.16415	3.369656	-1.00392	H	9.638496	0.325859	1.60717
H	-9.22501	2.450824	0.054434	C	14.3351	-1.3682	1.855046
H	-7.1396	4.484718	1.015085	C	13.42696	-1.82972	2.763116
H	-8.21761	3.5683	2.054001	C	12.06833	-1.77601	2.306249
H	-10.217	4.669854	0.95862	C	11.9659	-1.26277	1.027642
H	-9.12986	5.588554	-0.09307	S	13.55783	-0.83832	0.400788
C	-8.63815	-1.80985	4.171266	H	13.70651	-2.20758	3.74192
C	-9.77276	-2.58077	4.435886	C	10.91365	-2.28977	3.133482
C	-10.8981	-2.80529	3.638952	C	10.93628	-3.81938	3.327924
C	-11.1886	-2.28818	2.372782	C	9.774709	-4.32098	4.190897
C	-10.4295	-1.44295	1.567894	H	10.92925	-1.80731	4.121886
C	-9.06243	-0.91796	1.84952	H	9.964992	-2.00623	2.665873
C	-8.32418	-1.08308	3.01851	H	11.89049	-4.11626	3.783454
C	-8.66569	-0.1603	0.714083	H	10.90526	-4.30206	2.342481
C	-9.73141	-0.19675	-0.20722	H	8.807397	-4.06698	3.740593
C	-10.8063	-0.96003	0.285797	H	9.80094	-3.87314	5.192133
H	-7.89191	-1.77856	4.961736	H	-15.5638	-1.117	-1.12701
H	-9.78147	-3.07854	5.404346	H	15.41092	-1.30851	1.953627
H	-11.6561	-3.45967	4.063175	H	9.81032	-5.40961	4.311902
H	-12.1464	-2.58862	1.95273	H	9.544431	5.817117	-1.38922
H	-7.36372	-0.57221	3.036695	H	1.391426	-3.80694	-1.30986
H	-9.72349	0.295173	-1.17349	H	0.719969	-5.14115	-3.33019
C	-14.487	-1.21807	-1.09685	H	0.376236	6.45618	0.236142
C	-13.6582	-1.72729	-2.05409	H	-1.64627	6.931206	-2.05312
C	-12.2719	-1.72208	-1.68604	H	-9.12305	5.875653	1.654435

C	-12.0669	-1.19641	-0.42489	H	-10.2898	-5.46732	-3.77687

Cartesian coordinates of the DFT optimized ground-state of protonated BTAz-1

C	-2.66199	-0.05019	1.294945	C	3.33488	-0.5176	0.245912
C	-1.1537	3.778062	-0.46078	C	-3.57485	-0.03284	2.323853
C	-0.06326	3.940897	-1.30839	C	-4.91953	-0.49892	2.167404
C	0.992124	3.047798	-1.5567	C	-5.37772	-0.99117	0.9736
C	1.236697	1.79423	-1.00852	C	-4.471	-1.02528	-0.1252
C	0.474407	1.093044	-0.05728	C	-3.10948	-0.5546	0.031789
C	-0.75564	1.504624	0.531723	N	-2.37585	-0.63975	-1.08426
C	-1.4666	2.680571	0.356097	S	-3.36801	-1.28112	-2.2361
C	-1.226	0.412868	1.480351	N	-4.74089	-1.46247	-1.36139
C	-0.1651	-0.63452	1.30285	N	3.657921	0.716999	0.653119
C	0.815927	-0.23888	0.451453	S	5.305677	0.77766	0.673199
H	-1.86145	4.602819	-0.4309	N	5.65344	-0.74098	0.170156
H	-0.02526	4.877378	-1.85923	H	0.898213	-2.77165	-0.45278
H	1.72706	3.388193	-2.2822	H	2.852043	-4.18985	-0.93365
H	2.13136	1.29154	-1.35816	H	5.17402	-3.31988	-0.67138
H	-2.39304	2.758493	0.921891	H	-3.27241	0.337481	3.300543
C	2.005959	-1.03787	0.09658	H	-5.5816	-0.4576	3.026592
C	1.890174	-2.34875	-0.32065	H	-6.39344	-1.34833	0.844336
C	3.02399	-3.1703	-0.60311	H	-0.18122	-1.57556	1.841199
C	4.306044	-2.7032	-0.46558	H	-1.14569	0.808833	2.507228
C	4.48237	-1.35851	-0.0321				

Cartesian coordinates of the DFT optimized ground-state of protonated BTAz-2

C	-6.6071	-1.75816	-0.46294	H	4.331097	1.868155	-1.58991
C	-5.22312	-1.45332	-0.09618	C	1.671798	2.781684	-1.30161
C	-4.18573	-2.34559	0.084786	C	2.224951	4.140239	-0.8219
C	-2.92927	-1.76165	0.415298	C	1.543681	5.332535	-1.50506
C	-3.02241	-0.38606	0.481636	C	2.071876	6.691329	-1.02653
S	-4.64266	0.180739	0.159788	H	1.786564	2.715077	-2.39222
H	-4.31335	-3.41933	-0.00076	H	0.594242	2.749493	-1.10594
C	-1.68619	-2.59105	0.635232	H	3.306976	4.181025	-1.00592
C	-1.09785	-3.1751	-0.66582	H	2.099537	4.213485	0.267536
C	0.162441	-4.01542	-0.42674	H	0.458447	5.282057	-1.32994
C	0.743249	-4.61852	-1.71241	H	1.678664	5.25188	-2.59359
H	-0.9152	-1.99693	1.139685	H	3.157323	6.739389	-1.19726
H	-1.92618	-3.41728	1.318355	H	1.932128	6.772601	0.061782
H	-0.87009	-2.35303	-1.35873	C	1.396549	7.884025	-1.71595
H	-1.862	-3.78682	-1.16407	C	1.916567	9.244309	-1.23375
H	-0.06967	-4.82392	0.282244	C	1.243401	10.43661	-1.92577
H	0.927932	-3.3926	0.060398	C	1.765494	11.79127	-1.43674
H	0.969457	-3.80976	-2.42305	H	1.542247	7.804068	-2.8033
H	-0.02071	-5.24365	-2.19729	H	0.309932	7.831313	-1.55112
C	2.008076	-5.45405	-1.47615	H	3.003314	9.296963	-1.39679
C	2.591653	-6.05713	-2.7602	H	1.769095	9.325622	-0.14628

C	3.858379	-6.89003	-2.52521	H	0.157214	10.38225	-1.76477
C	4.435286	-7.48773	-3.81232	H	1.393724	10.35624	-3.01168
H	2.770425	-4.8277	-0.98922	H	1.26564	12.62045	-1.94946
H	1.780848	-6.26272	-0.76572	H	2.842948	11.88969	-1.61703
H	2.816629	-5.24897	-3.47242	H	1.597764	11.91606	-0.35987
H	1.830174	-6.6851	-3.24593	C	5.556594	-0.37734	-0.30061
H	3.633198	-7.6984	-1.81512	C	6.424607	-0.03884	-1.32597
H	4.619053	-6.26231	-2.03902	C	7.744956	-0.563	-1.43534
H	5.336457	-8.07712	-3.61005	C	8.249446	-1.46185	-0.5303
H	4.704955	-6.70234	-4.5292	C	7.400692	-1.86337	0.538012
H	3.709553	-8.1476	-4.30299	C	6.057257	-1.32662	0.65764
C	-1.87803	0.558653	4.702586	C	-6.99416	-3.02801	-0.85911
C	-0.60861	0.668391	5.261101	C	-8.33488	-3.36237	-1.20615
C	0.625835	0.810772	4.605117	C	-9.34709	-2.43671	-1.18324
C	0.904735	0.8295	3.243444	C	-9.01231	-1.10962	-0.79729
C	0.009145	0.700889	2.165879	C	-7.64884	-0.76628	-0.43782
C	-1.41231	0.61871	2.235347	N	-7.49576	0.518462	-0.10402
C	-2.23912	0.559141	3.345773	S	-8.97954	1.220529	-0.24273
C	-1.96199	0.640051	0.815323	N	-9.85924	-0.07499	-0.72527
C	-0.7095	0.6233	-0.00894	N	5.386139	-1.80577	1.709244
C	0.419456	0.686507	0.753796	S	6.399593	-2.85633	2.474081
H	-2.70245	0.476177	5.406684	N	7.714568	-2.73569	1.503956
H	-0.56482	0.658264	6.347313	H	6.092079	0.647955	-2.09739
H	1.489678	0.916531	5.257181	H	8.356654	-0.23751	-2.2713
H	1.949751	0.949857	2.971718	H	9.250526	-1.87067	-0.60871
H	-3.30413	0.486949	3.133014	H	-6.24979	-3.81488	-0.92337
C	4.215992	0.203298	-0.20931	H	-8.54596	-4.38536	-1.50278
C	3.721874	1.284189	-0.90908	H	-10.3689	-2.68126	-1.4508
C	2.355498	1.596917	-0.66221	H	-0.72972	0.570672	-1.09093
C	1.79895	0.731843	0.264838	H	-2.42621	1.636924	0.693135
S	2.964198	-0.45908	0.823642				

Cartesian coordinates of the DFT optimized ground-state of protonated BTAz-3

N	1.468735	-1.55415	-0.43034	H	9.207683	-1.14488	5.642174
C	0.890928	-0.36723	-0.23757	C	-2.80752	0.67414	0.233908
C	-0.55549	-0.45149	-0.10852	C	-3.66455	1.726336	0.503555
N	-1.02227	-1.69904	-0.20979	C	-5.04591	1.393117	0.552368
S	0.276907	-2.68132	-0.44755	C	-5.24665	0.049245	0.300199
C	-1.35869	0.71789	0.105289	S	-3.74212	-0.79837	0.030516
C	-0.64317	1.909832	0.180541	H	-3.31541	2.739417	0.670952
C	0.757065	1.994745	0.062137	C	-6.11152	2.430203	0.819991
C	1.585921	0.894222	-0.15934	C	-6.3689	3.369292	-0.37709
H	-1.17958	2.840198	0.336597	C	-7.43621	4.425729	-0.07927
H	1.201063	2.979888	0.151161	H	-7.05395	1.948421	1.103525
C	3.020814	1.024865	-0.30028	H	-5.809	3.035765	1.685286
C	3.743239	2.208285	-0.36708	H	-6.66953	2.768717	-1.24585
C	5.14246	2.060859	-0.50163	H	-5.42795	3.858905	-0.65865

C	5.521181	0.718591	-0.5385	H	-7.14799	5.054217	0.771991
S	4.125197	-0.33536	-0.40405	H	-8.40113	3.961708	0.159749
H	3.270379	3.184309	-0.34596	C	-7.07965	-1.50199	4.057729
C	6.06956	3.242144	-0.67699	C	-8.40346	-1.37655	4.491634
C	5.765527	4.074802	-1.93925	C	-9.53637	-1.03729	3.74487
C	6.716912	5.263946	-2.0997	C	-9.63926	-0.70158	2.392864
H	6.004847	3.895992	0.205	C	-8.61363	-0.60375	1.441453
H	7.105935	2.896163	-0.72847	C	-7.23175	-0.90771	1.621881
H	4.728621	4.435057	-1.90353	C	-6.56183	-1.30479	2.773157
H	5.831828	3.421811	-2.81904	C	-6.52617	-0.75801	0.281776
H	7.758761	4.930867	-2.17693	C	-7.63111	-0.26527	-0.60588
H	6.65008	5.946557	-1.24356	C	-8.82646	-0.20128	0.040295
C	6.990171	-2.61657	-3.25817	H	-6.35906	-1.8031	4.813985
C	8.215668	-3.2841	-3.31865	H	-8.57789	-1.58578	5.544063
C	9.379012	-3.06345	-2.57794	H	-10.4745	-1.03416	4.294898
C	9.619838	-2.09149	-1.60213	H	-10.6402	-0.48506	2.030294
C	8.763695	-1.11899	-1.09206	H	-5.49228	-1.47046	2.65704
C	7.330555	-0.91285	-1.42745	C	-12.2164	1.421495	-1.10329
C	6.600475	-1.57285	-2.41244	C	-11.9549	0.391843	-1.9585
C	6.860972	0.153861	-0.60288	C	-10.7477	-0.32182	-1.65882
C	7.954003	0.590291	0.178818	C	-10.1098	0.198112	-0.54805
C	9.107868	-0.15876	-0.09621	S	-10.9965	1.568016	0.11493
H	6.229676	-2.96036	-3.95521	H	-12.6004	0.139248	-2.79303
H	8.272848	-4.08905	-4.04921	C	-10.3009	-1.52225	-2.4579
H	10.21438	-3.72352	-2.79846	C	-11.2619	-2.72416	-2.34404
H	10.62129	-2.09246	-1.17742	C	-10.8062	-3.91965	-3.18538
H	5.577856	-1.22845	-2.54718	H	-10.2146	-1.23592	-3.51542
C	12.82933	0.558055	0.966881	H	-9.29939	-1.83618	-2.1431
C	12.1173	0.344071	2.111287	H	-12.2688	-2.41692	-2.65408
C	10.73281	0.045633	1.887307	H	-11.3441	-3.01695	-1.28892
C	10.4124	0.03645	0.542844	H	-9.81512	-4.27259	-2.87484
S	11.8285	0.407886	-0.43771	H	-10.7472	-3.65811	-4.24853
H	12.55905	0.392374	3.101723	H	7.906556	1.388292	0.91037
C	9.782849	-0.28299	3.014634	H	13.87985	0.796095	0.865294
C	10.10616	-1.62084	3.710636	H	-7.46684	-0.00065	-1.6438
C	9.155897	-1.92493	4.872589	H	-13.0487	2.112632	-1.11887
H	9.81358	0.521938	3.763381	H	-6.26274	-1.78011	-0.04752
H	8.754374	-0.31846	2.639732	H	9.404362	-2.87979	5.34904
H	11.14144	-1.60205	4.075689	H	6.483473	5.838372	-3.00286
H	10.05916	-2.42745	2.967578	H	-7.58934	5.083561	-0.94121
H	8.115334	-1.98384	4.530201	H	-11.5036	-4.75812	-3.08718

Cartesian coordinates of the DFT optimized ground-state of protonated BTAz-4

C	1.421424	0.250647	-0.17928	H	-14.2881	-1.21674	-3.19177
C	1.193323	1.598419	0.230394	C	-11.9882	-2.63039	-2.25946
C	-0.07948	2.114362	0.439459	C	-12.912	-3.81646	-1.91139
C	-1.1776	1.250479	0.24839	C	-12.3484	-5.15748	-2.38961

C	-0.94912	-0.09825	-0.15	H	-11.827	-2.61317	-3.34636
C	0.323187	-0.61468	-0.36344	H	-11.0049	-2.80013	-1.80677
C	2.810926	-0.02364	-0.36515	H	-13.9011	-3.65126	-2.35715
C	3.630503	1.045489	-0.09517	H	-13.0678	-3.84064	-0.82468
S	2.705643	2.47099	0.423948	H	-11.3729	-5.36641	-1.93357
S	-2.46115	-0.97214	-0.3463	H	-12.2147	-5.16707	-3.47784
C	-3.38247	0.459467	0.152989	C	5.067364	1.119314	-0.18229
C	-2.56727	1.529125	0.424921	C	5.88007	2.230069	-0.08157
O	-0.27043	3.409263	0.853943	C	7.270197	1.973108	-0.23046
O	0.488156	-1.91091	-0.78321	C	7.535753	0.62664	-0.44976
H	3.181431	-0.97895	-0.7185	S	6.043934	-0.31046	-0.45049
H	-2.93362	2.485295	0.779655	H	5.483768	3.228579	0.075856
C	0.818034	-2.85933	0.256687	C	8.299079	3.079753	-0.23067
C	0.9699	-4.22787	-0.38851	C	8.120402	4.076735	-1.39422
C	1.322831	-5.31308	0.633937	C	9.160503	5.200552	-1.36637
H	1.748405	-2.5507	0.752366	H	8.244287	3.629463	0.720192
H	0.018389	-2.86268	1.010394	H	9.305234	2.653743	-0.28444
H	1.746227	-4.16606	-1.16109	H	7.111057	4.507818	-1.35884
H	0.545986	-5.40948	1.402041	H	8.186415	3.529597	-2.34346
H	2.268905	-5.09327	1.142934	H	10.17922	4.800667	-1.43593
C	-0.37555	4.383009	-0.20946	H	9.094797	5.780533	-0.43764
C	-0.53253	5.756756	0.423313	C	8.775931	-2.34456	-3.65526
C	-0.66822	6.863382	-0.62804	C	9.93728	-3.10594	-3.80729
H	0.524912	4.3389	-0.8364	C	11.09316	-3.12071	-3.02356
H	-1.24026	4.136073	-0.84199	C	11.39341	-2.34884	-1.89654
H	-1.41223	5.743684	1.079079	C	10.61576	-1.395	-1.24597
H	0.21277	6.907446	-1.27916	C	9.218379	-1.00083	-1.56563
H	-0.77603	7.842258	-0.15006	C	8.458845	-1.42007	-2.65454
C	-4.82774	0.43105	0.229331	C	8.82149	-0.04627	-0.58201
C	-5.70447	1.495548	0.211904	C	9.921451	0.149161	0.280372
C	-7.08128	1.142305	0.323688	C	11.01331	-0.64853	-0.09817
C	-7.25281	-0.22449	0.417983	H	8.008247	-2.49711	-4.41014
S	-5.71962	-1.06741	0.387997	H	9.94272	-3.78266	-4.65992
H	-5.36858	2.52104	0.099858	H	11.8707	-3.81256	-3.33816
C	-8.18021	2.178687	0.295898	H	12.37705	-2.51642	-1.46342
C	-8.39342	2.808179	-1.09641	H	7.476182	-0.96227	-2.74257
C	-9.49642	3.869918	-1.10147	H	9.921658	0.819459	1.131792
H	-9.12564	1.74405	0.640101	C	14.74895	-0.4818	1.12991
H	-7.93466	2.975615	1.011306	C	13.97995	-0.78489	2.216075
H	-8.63565	2.013955	-1.81477	C	12.58147	-0.90285	1.923852
H	-7.44941	3.250092	-1.43959	C	12.30785	-0.68373	0.586298
H	-9.26754	4.686089	-0.40558	S	13.78718	-0.32215	-0.30053
H	-10.4632	3.442182	-0.8084	H	14.38971	-0.92662	3.211293
C	-9.43195	-0.7759	4.313024	C	11.5678	-1.2958	2.972299
C	-10.7872	-0.65115	4.578819	C	11.72298	-2.75459	3.448967
C	-11.8615	-0.61683	3.661703	C	10.71093	-3.13063	4.535068
C	-11.8351	-0.64261	2.277598	H	11.66428	-0.62734	3.840126
C	-10.7131	-0.70399	1.421269	H	10.55295	-1.15677	2.585109

C	-9.34978	-0.86129	1.802346	H	12.74303	-2.90975	3.824301
C	-8.78556	-0.89665	3.067332	H	11.61054	-3.42284	2.585349
C	-8.52078	-1.03899	0.532617	H	9.680934	-3.01576	4.175494
C	-9.54252	-0.83947	-0.54838	H	10.82474	-2.49502	5.421911
C	-10.7972	-0.67	-0.04355	H	-14.9498	1.078625	-2.0993
H	-8.77713	-0.79773	5.180986	H	15.82066	-0.34032	1.085372
H	-11.0643	-0.58632	5.627867	H	-8.22775	-2.10468	0.520106
H	-12.8509	-0.55542	4.108649	H	10.83871	-4.17137	4.853004
H	-12.7998	-0.60388	1.779128	H	9.016963	5.893292	-2.20285
H	-7.70417	-1.01252	3.098671	H	1.428284	-6.28701	0.145375
H	-9.28285	-0.83734	-1.6001	H	0.034118	-4.4783	-0.90309
C	-14.1043	0.454505	-1.84222	H	0.335265	5.94693	1.066217
C	-13.7332	-0.73703	-2.39241	H	-1.54631	6.70643	-1.26616
C	-12.5409	-1.29496	-1.82347	H	-9.6161	4.306912	-2.09838
C	-12.0269	-0.49026	-0.82396	H	-13.0205	-5.9819	-2.12965
S	-13.011	0.952539	-0.59696				

Excitation energies and oscillator strengths from the ground-state structures (S_0) of BTAzs and protonated BTAzs

BTAz-2

Excited State 1: Singlet-A 2.1814 eV 568.37 nm f=0.0105 <S**2>=0.000
208 ->210 0.70433
Excited State 2: Singlet-A 2.6981 eV 459.52 nm f=0.2358 <S**2>=0.000
207 ->210 0.69687
Excited State 3: Singlet-A 2.7185 eV 456.08 nm f=0.0013 <S**2>=0.000
207 ->209 0.69568
Excited State 4: Singlet-A 2.8607 eV 433.41 nm f=0.0002 <S**2>=0.000
207 ->211 0.67675
208 ->212 -0.18565
Excited State 5: Singlet-A 3.2041 eV 386.96 nm f=0.0982 <S**2>=0.000
203 ->211 0.13771
205 ->211 -0.12593
206 ->210 -0.24082
207 ->211 0.16765
208 ->212 0.60917

***

BTAz-3

Excited State 1: Singlet-A 2.0654 eV 600.29 nm f=0.0085 <S**2>=0.000
231 -> 236 0.12427
232 -> 235 -0.37847
233 -> 236 0.57790
Excited State 2: Singlet-A 2.0656 eV 600.24 nm f=0.0001 <S**2>=0.000
231 -> 235 0.12419
232 -> 236 -0.37814
233 -> 235 0.57794
Excited State 3: Singlet-A 2.2138 eV 560.05 nm f=0.0052 <S**2>=0.000
232 -> 234 0.70418
Excited State 4: Singlet-A 2.5654 eV 483.29 nm f=0.0844 <S**2>=0.000
231 -> 234 0.69451
Excited State 5: Singlet-A 2.6008 eV 476.71 nm f=0.0004 <S**2>=0.000
231 -> 235 -0.26201
232 -> 236 0.51312
233 -> 235 0.39745
Excited State 6: Singlet-A 2.6013 eV 476.63 nm f=0.0001 <S**2>=0.000
231 -> 236 -0.25881

232 -> 235 0.50907
233 -> 236 0.39381
Excited State 7: Singlet-A 2.9779 eV 416.35 nm f=0.1228 <S**2>=0.000
230 -> 235 -0.16209
231 -> 236 0.44615
232 -> 235 0.23556
233 -> 237 0.44476
Excited State 8: Singlet-A 3.0539 eV 405.98 nm f=0.2957 <S**2>=0.000
231 -> 236 -0.42131
232 -> 235 -0.17123
233 -> 237 0.51224
233 -> 239 -0.10091

Excited State 9: Singlet-A 3.4744 eV 356.85 nm f=0.4237 <S**2>=0.000
225 -> 234 -0.15552
229 -> 234 -0.21152
230 -> 235 -0.13796
232 -> 238 0.23611
233 -> 239 0.56513

***

BTAz-4

Excited State 1: Singlet-A 2.0915 eV 592.81 nm f=0.0063 <S**2>=0.000
277 -> 281 0.20896
278 -> 281 -0.44702
279 -> 281 0.49822
Excited State 2: Singlet-A 2.5097 eV 494.03 nm f=0.0019 <S**2>=0.000
277 -> 280 -0.35979
278 -> 280 -0.36854
279 -> 280 0.46138
Excited State 3: Singlet-A 2.5338 eV 489.31 nm f=0.0016 <S**2>=0.000
277 -> 281 -0.29462
278 -> 281 0.39453
279 -> 281 0.49080
Excited State 4: Singlet-A 2.6771 eV 463.13 nm f=1.5955 <S**2>=0.000
279 -> 282 0.69602
Excited State 5: Singlet-A 2.8476 eV 435.40 nm f=0.0080 <S**2>=0.000
275 -> 280 -0.11870
277 -> 280 0.51502
278 -> 280 -0.44671

***

Protonated BTAz-2

Excited State 1: Singlet-A 1.2022 eV 1031.29 nm f=0.0015 <S**2>=0.000
207 ->209 0.66903
208 ->210 -0.21835
Excited State 2: Singlet-A 1.2650 eV 980.11 nm f=0.0325 <S**2>=0.000
207 ->209 0.21872
208 ->210 0.66754
Excited State 3: Singlet-A 1.3337 eV 929.65 nm f=0.0063 <S**2>=0.000
207 ->210 0.70312
Excited State 4: Singlet-A 2.1079 eV 588.18 nm f=0.0004 <S**2>=0.000
206 ->209 0.69652
Excited State 5: Singlet-A 2.1955 eV 564.72 nm f=0.0003 <S**2>=0.000
205 ->209 0.69946
Excited State 6: Singlet-A 2.2638 eV 547.69 nm f=0.0018 <S**2>=0.000
206 ->210 0.69732
Excited State 7: Singlet-A 2.3606 eV 525.22 nm f=0.0028 <S**2>=0.000
205 ->210 0.69961
Excited State 8: Singlet-A 2.4567 eV 504.68 nm f=0.0003 <S**2>=0.000
204 ->209 0.69342

***

Protonated BTAz-3

Excited State 1: Singlet-A 0.3824 eV 3241.90 nm f=0.1591 <S**2>=0.000

233 -> 234 0.44119
233 -> 235 0.64904
233 <- 234 -0.24373
233 <- 235 -0.23516
Excited State 2: Singlet-A 0.7380 eV 1680.00 nm f=0.0009 <S**2>=0.000
232 -> 234 0.67561
232 -> 235 -0.14458
Excited State 3: Singlet-A 0.8485 eV 1461.15 nm f=0.0133 <S**2>=0.000
232 -> 234 0.15520
232 -> 235 0.68514
Excited State 4: Singlet-A 1.3146 eV 943.16 nm f=0.0020 <S**2>=0.000
230 -> 234 -0.25370
231 -> 234 0.63065
232 -> 234 -0.11953
Excited State 5: Singlet-A 1.4010 eV 884.99 nm f=0.0174 <S**2>=0.000
230 -> 235 -0.23814
231 -> 235 0.63479
233 -> 236 0.13737
Excited State 6: Singlet-A 1.4786 eV 838.51 nm f=0.0008 <S**2>=0.000
230 -> 234 0.64175
231 -> 234 0.27367
Excited State 7: Singlet-A 1.5536 eV 798.04 nm f=0.0053 <S**2>=0.000
230 -> 235 0.63871
231 -> 235 0.27056
Excited State 8: Singlet-A 1.6216 eV 764.60 nm f=0.3237 <S**2>=0.000
230 -> 235 0.13293
233 -> 236 0.68088
Excited State 9: Singlet-A 1.8098 eV 685.07 nm f=0.0011 <S**2>=0.000
229 -> 234 0.68109
229 -> 235 0.10011
Excited State 10: Singlet-A 1.8761 eV 660.87 nm f=0.0002 <S**2>=0.000
228 -> 234 0.65273
229 -> 235 0.22223

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Protonated BTAz-4

Excited State 1: Singlet-A 0.2960 eV 4187.95 nm f=0.0929 <S**2>=0.000
279 -> 280 0.61049
279 -> 281 0.60261
279 <- 280 -0.48473
Excited State 2: Singlet-A 0.5211 eV 2379.24 nm f=0.0436 <S**2>=0.000
278 -> 280 0.68869
279 -> 280 0.13393
Excited State 3: Singlet-A 0.7447 eV 1664.80 nm f=0.0101 <S**2>=0.000
278 -> 281 0.69605
Excited State 4: Singlet-A 0.9308 eV 1331.98 nm f=0.0010 <S**2>=0.000
277 -> 280 0.69668
Excited State 5: Singlet-A 1.1913 eV 1040.76 nm f=0.0001 <S**2>=0.000
277 -> 281 0.69775
Excited State 6: Singlet-A 1.2536 eV 989.00 nm f=0.0068 <S**2>=0.000
274 -> 280 -0.19375
275 -> 280 -0.23448
276 -> 280 0.62061
Excited State 7: Singlet-A 1.4445 eV 858.31 nm f=0.0005 <S**2>=0.000
275 -> 280 0.64671
276 -> 280 0.27299
Excited State 8: Singlet-A 1.5170 eV 817.32 nm f=0.0080 <S**2>=0.000
274 -> 281 -0.19059
275 -> 281 -0.23612
276 -> 281 0.62008
Excited State 9: Singlet-A 1.6251 eV 762.95 nm f=0.0027 <S**2>=0.000
272 -> 280 -0.10934
273 -> 280 0.15043

274 -> 280 0.63506
275 -> 280 -0.14786
276 -> 280 0.16736
Excited State 10: Singlet-A 1.7250 eV 718.74 nm f=0.0003 <S**2>=0.000
275 -> 281 0.64275
276 -> 281 0.27670

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