Phenothiazine and phenothiazine-5,5dioxide-based push-pull derivatives: Synthesis, photophysical, electrochemical and computational studies

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Supporting Information

Experimental Section:

General methods

All the chemicals were used as received unless otherwise indicated. All oxygen or moisture-sensitive reactions were performed under an inert atmosphere. All the chemicals were purchased from commercial sources and used without further purification. ^{1}H NMR (400 MHz), ^{13}C NMR (100 MHz and 126 MHz), and HMBC NMR spectra were recorded on the Bruker Avance (III) 400 MHz or 500 MHz, using $CDCl_3$ as a solvent, and the chemical shifts were reported in parts per million (ppm) with TMS (0 ppm) and $CDCl_3$ (77.00 ppm) as standards. Tetramethylsilane (TMS) was used as reference for recording ^{1}H (of residual proton; δ = 7.26 ppm) and ^{13}C (of residual proton; δ = 77.0 ppm) spectra in $CDCl_3$. High-Resolution Mass Spectrometry (HRMS) was recorded on a Bruker-Daltonics micrOTOF-Q II mass spectrometer. Thermogravimetric analysis was performed on the Mettler Toledo thermal analysis system. UV-visible absorption spectra of all compounds in Dichloromethane were recorded on a Carry-100 Bio UV-visible Spectrophotometer. Cyclic voltammograms (CVs) were recorded on a PalmSens 4 electrochemical analyzer using Glassy carbon as a working electrode, Pt wire as the counter electrode, and Ag/AgCl as the reference electrode. The scan rate was 100 mV s^{-1} for cyclic voltammetry. A solution of tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) in CH_2Cl_2 (0.1 M) was used as the supporting electrolyte.

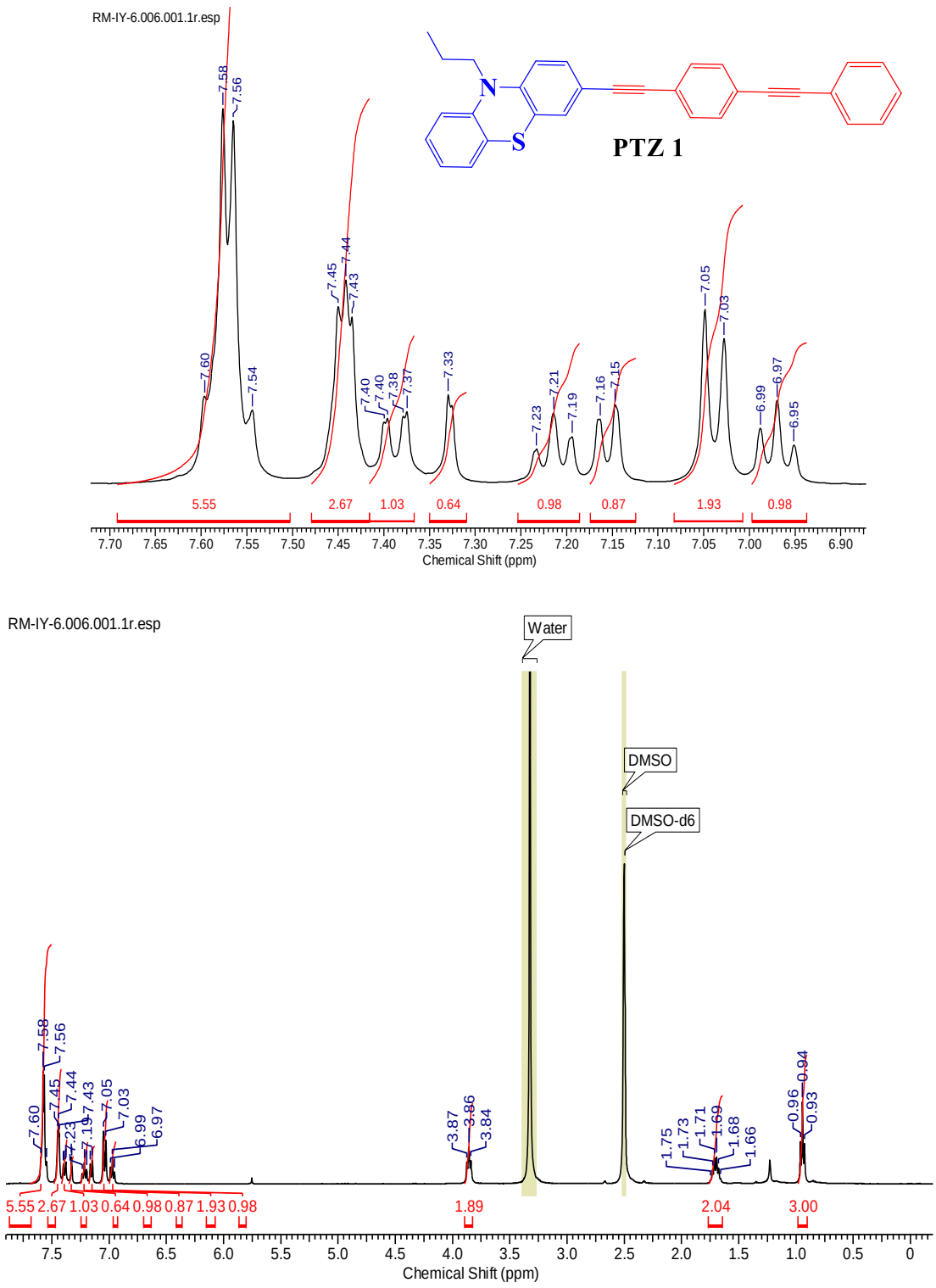


Figure S1. ^{1}H NMR spectrum of **PTZ 1**.

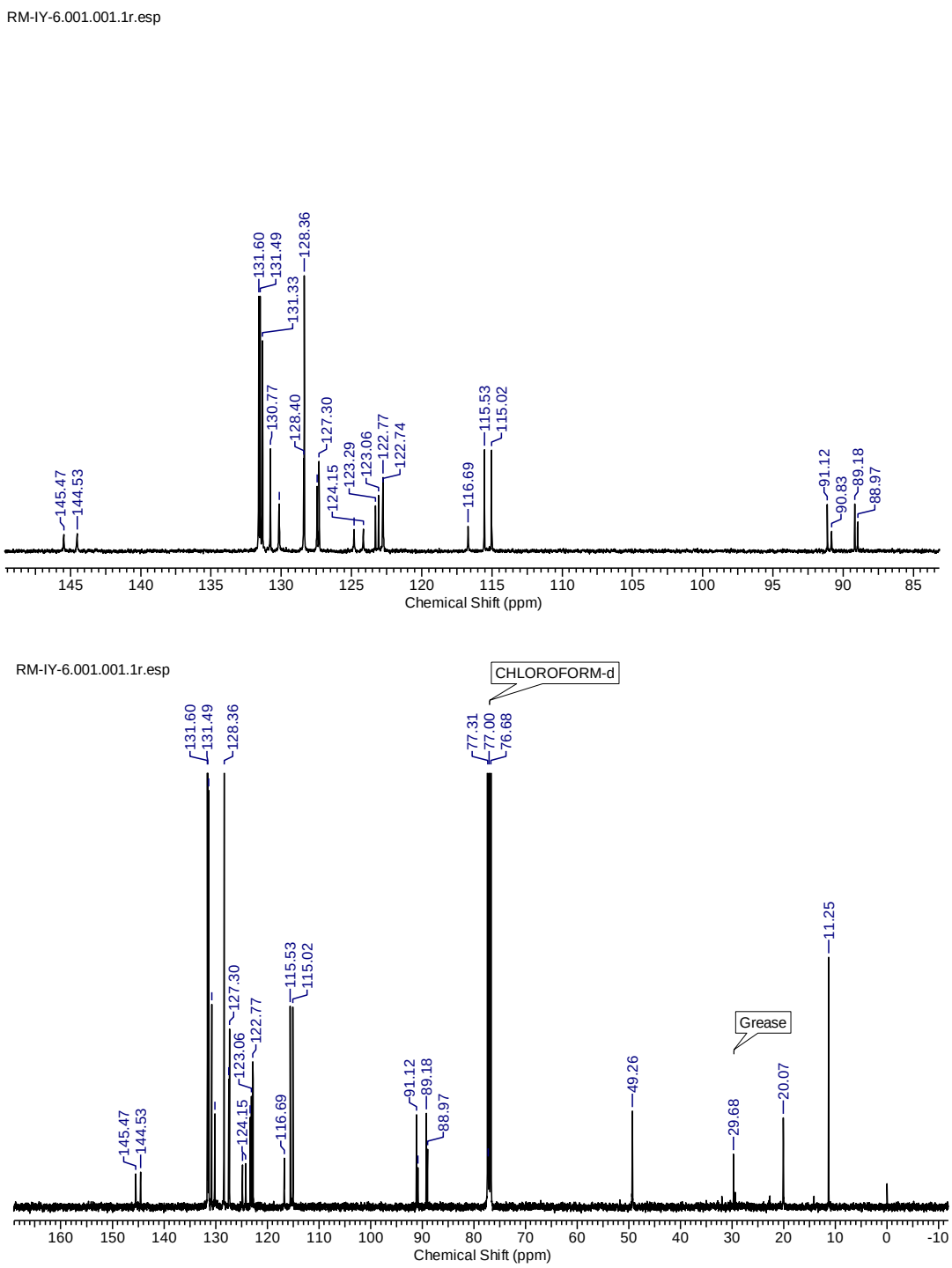


Figure S2. ^{13}C NMR spectrum of **PTZ 1**.

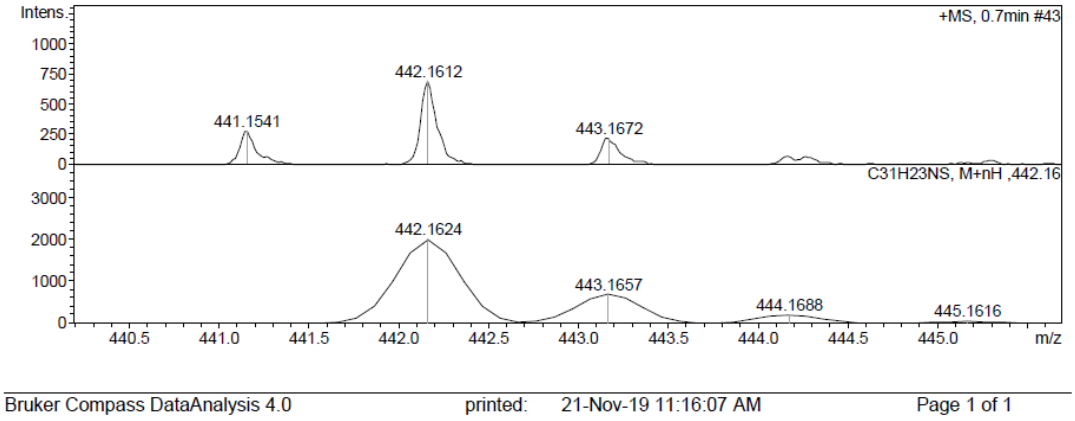


Figure S3. HRMS spectrum of **PTZ 1**.

RM-IY-C6A.001.001.1r.esp

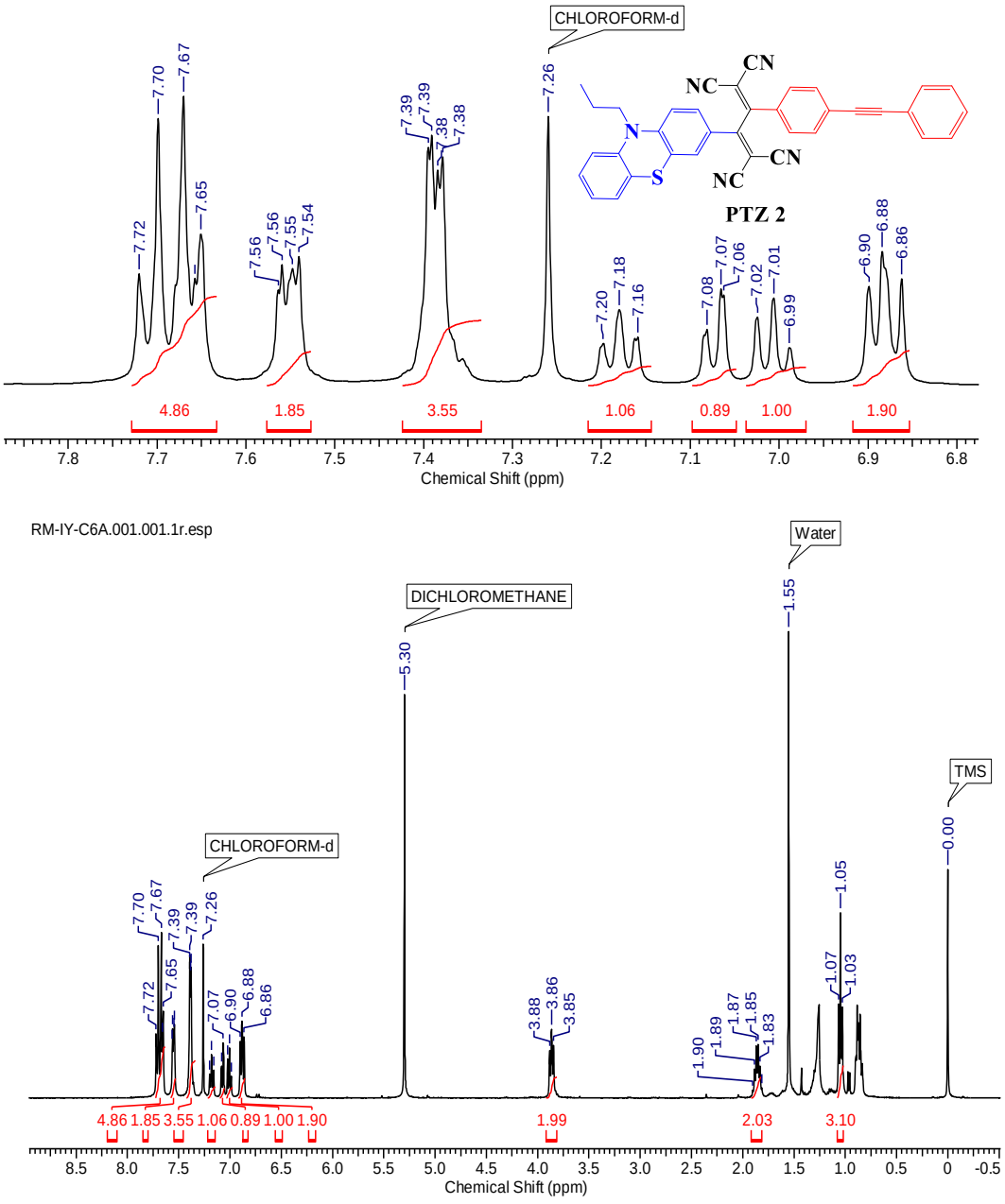


Figure S4. ^{1}H NMR spectrum of **PTZ 2**.

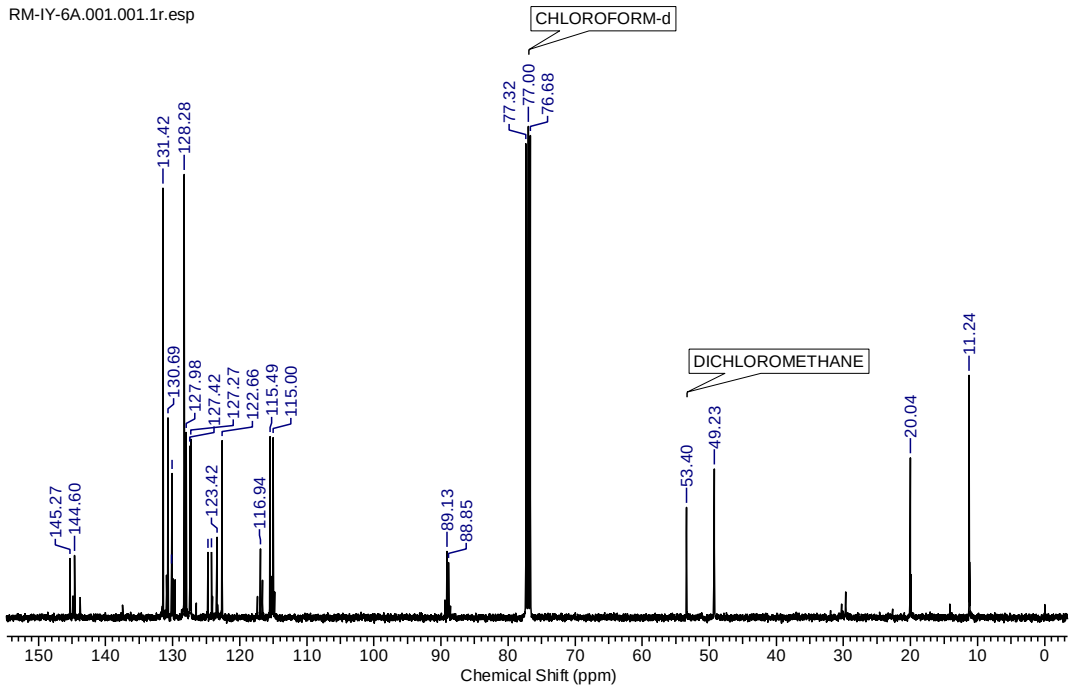


Figure S5. ^{13}C NMR spectrum of **PTZ 2**.

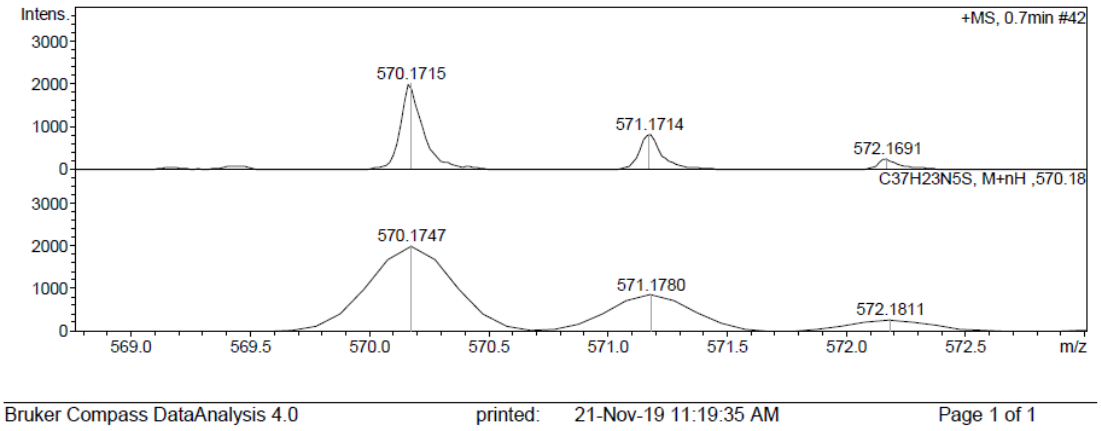


Figure S6. HRMS spectrum of **PTZ 2**.

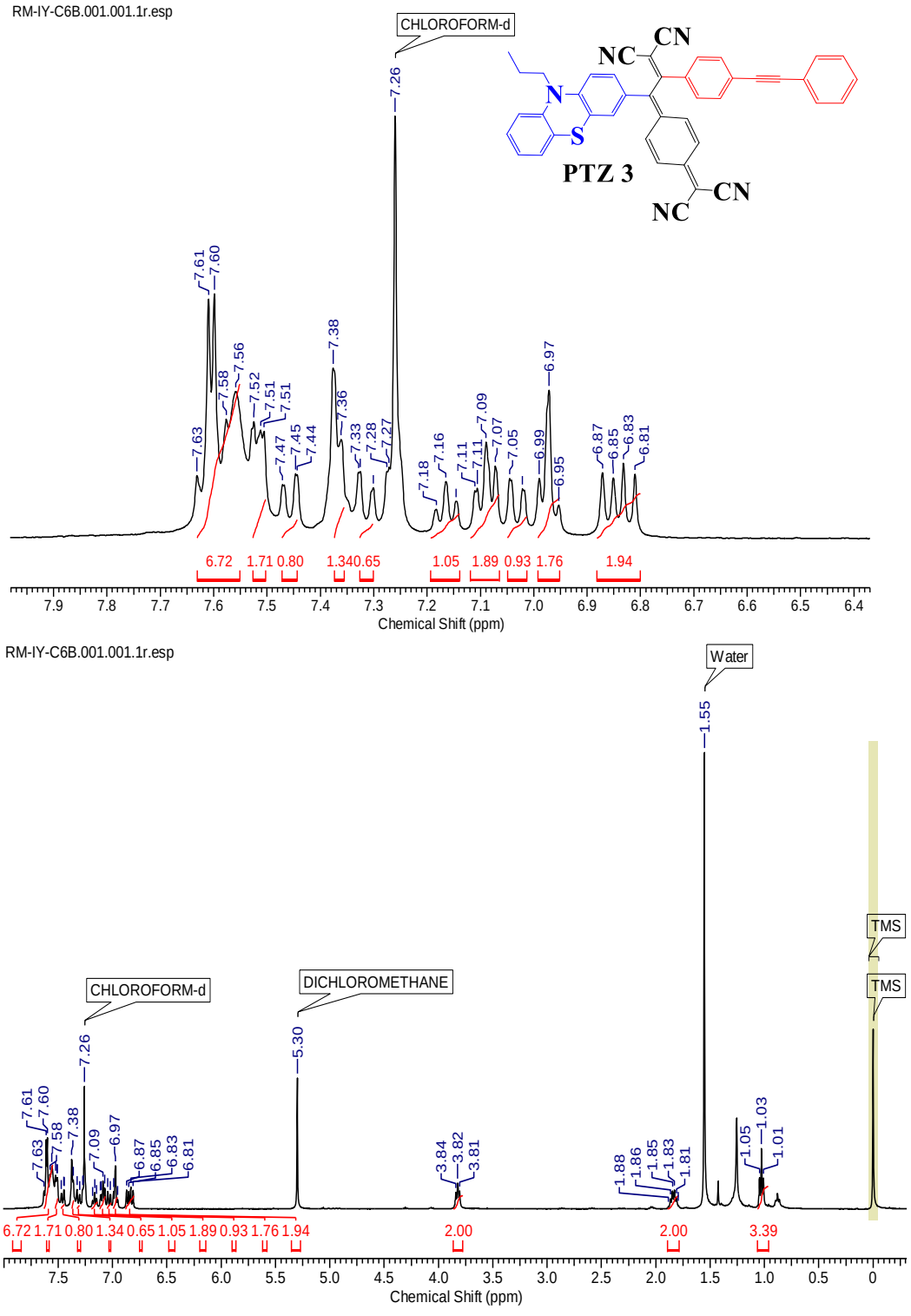


Figure S7. ^{1}H NMR spectrum of **PTZ 3**.

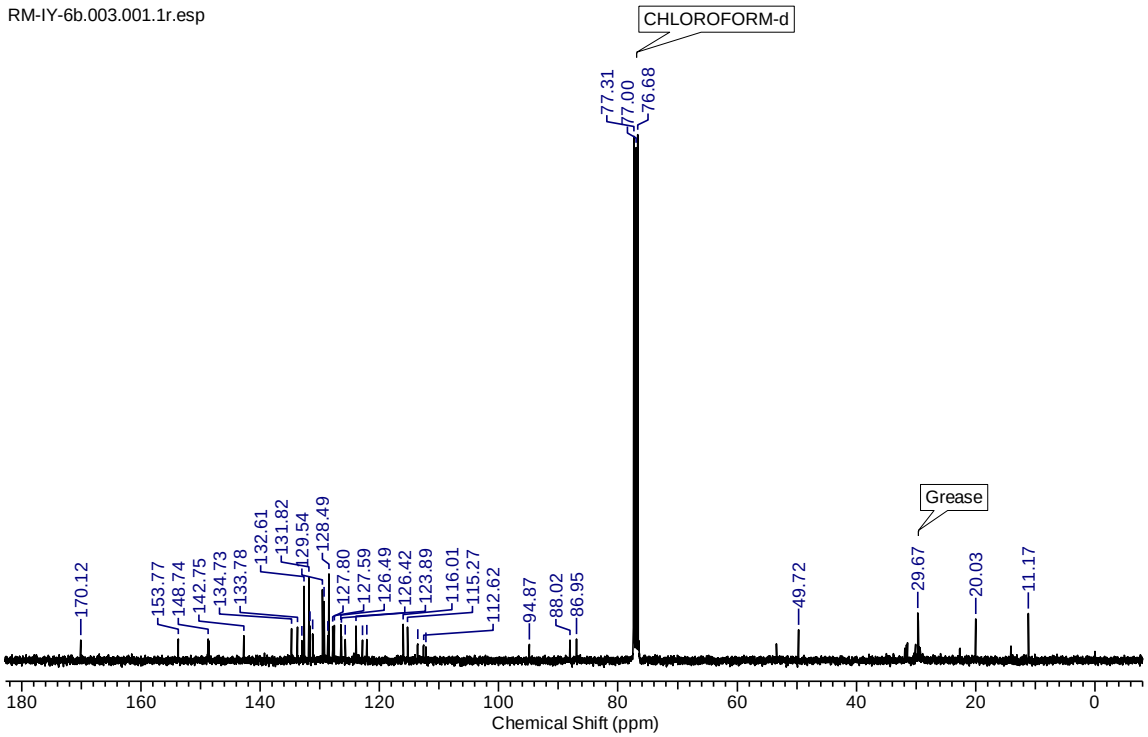


Figure S8. ^{13}C NMR spectrum of **PTZ 3**.

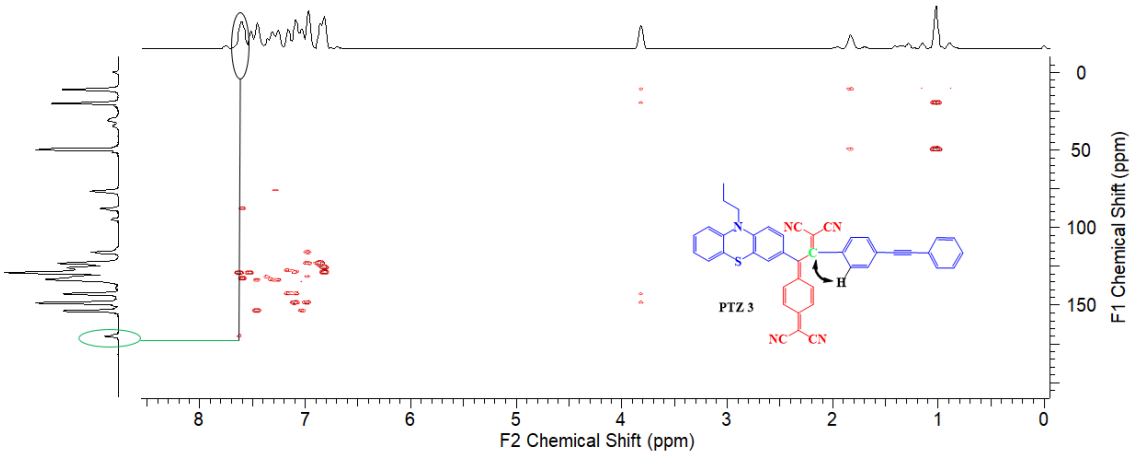


Figure S9. HMBC spectrum of **PTZ 3** in $CDCl_3$ solution.

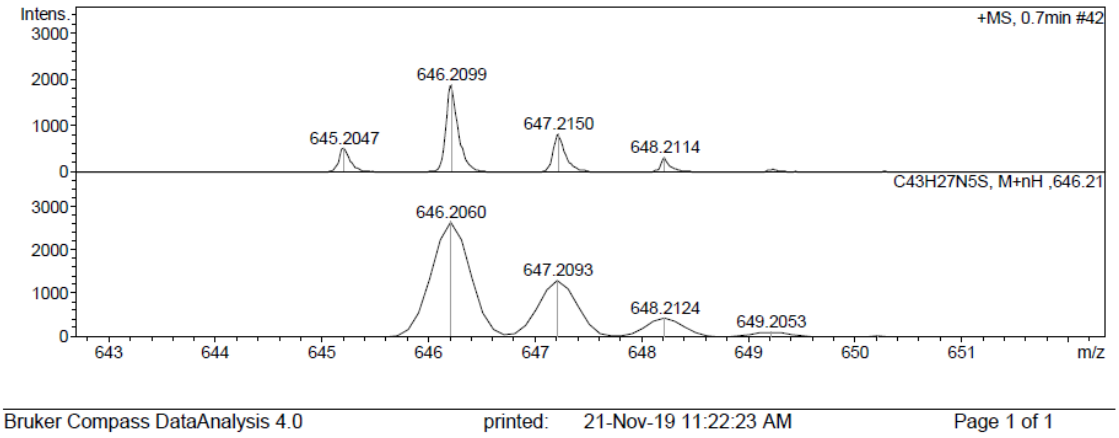


Figure S10. HRMS spectrum of **PTZ 3**.

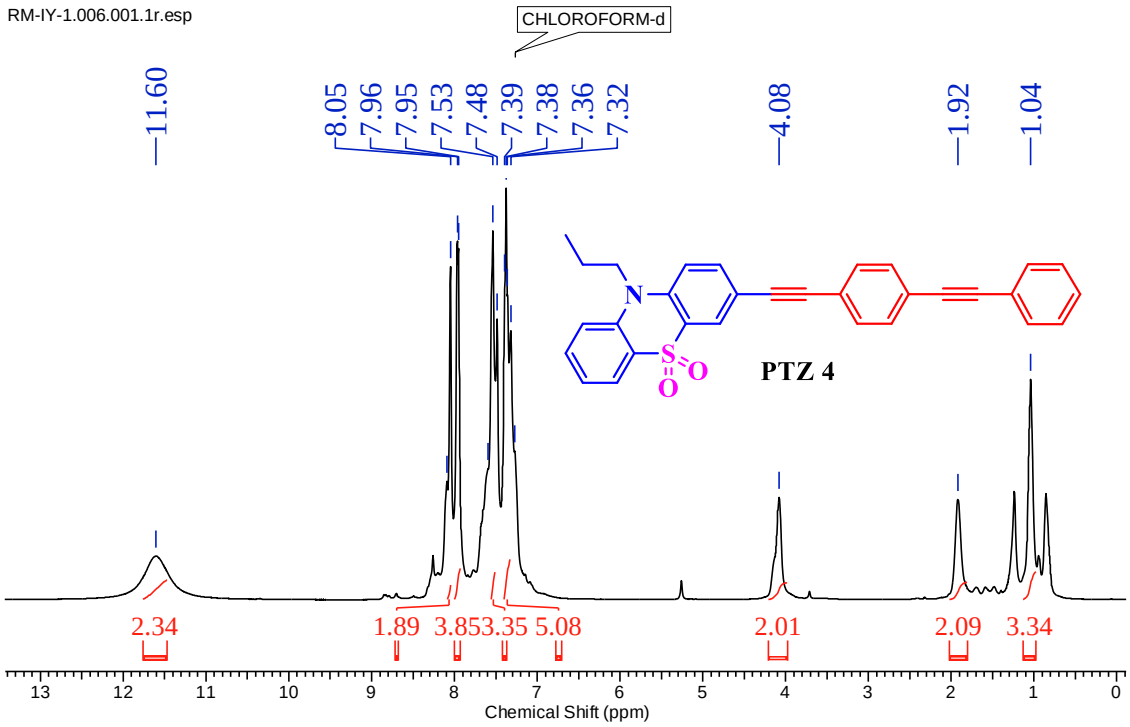


Figure S11. ^{1}H NMR spectrum of **PTZ 4**.

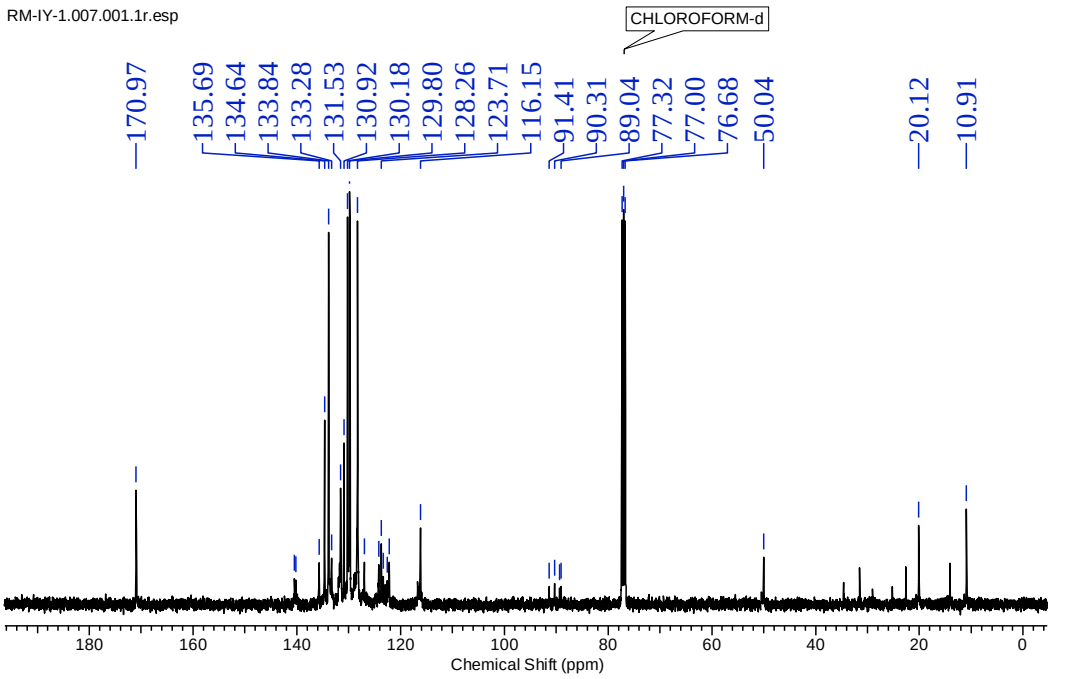


Figure S12. ^{13}C NMR spectrum of **PTZ 4**.

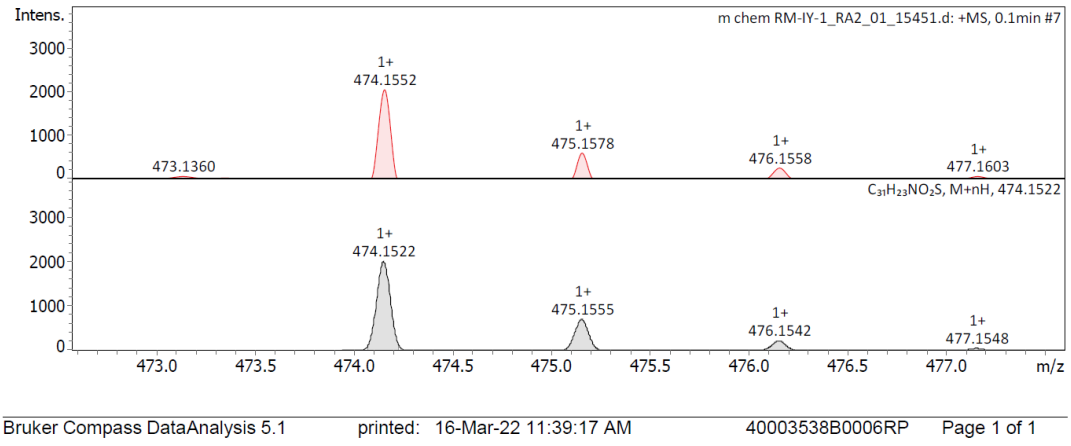


Figure S13. HRMS spectrum of **PTZ 4**.

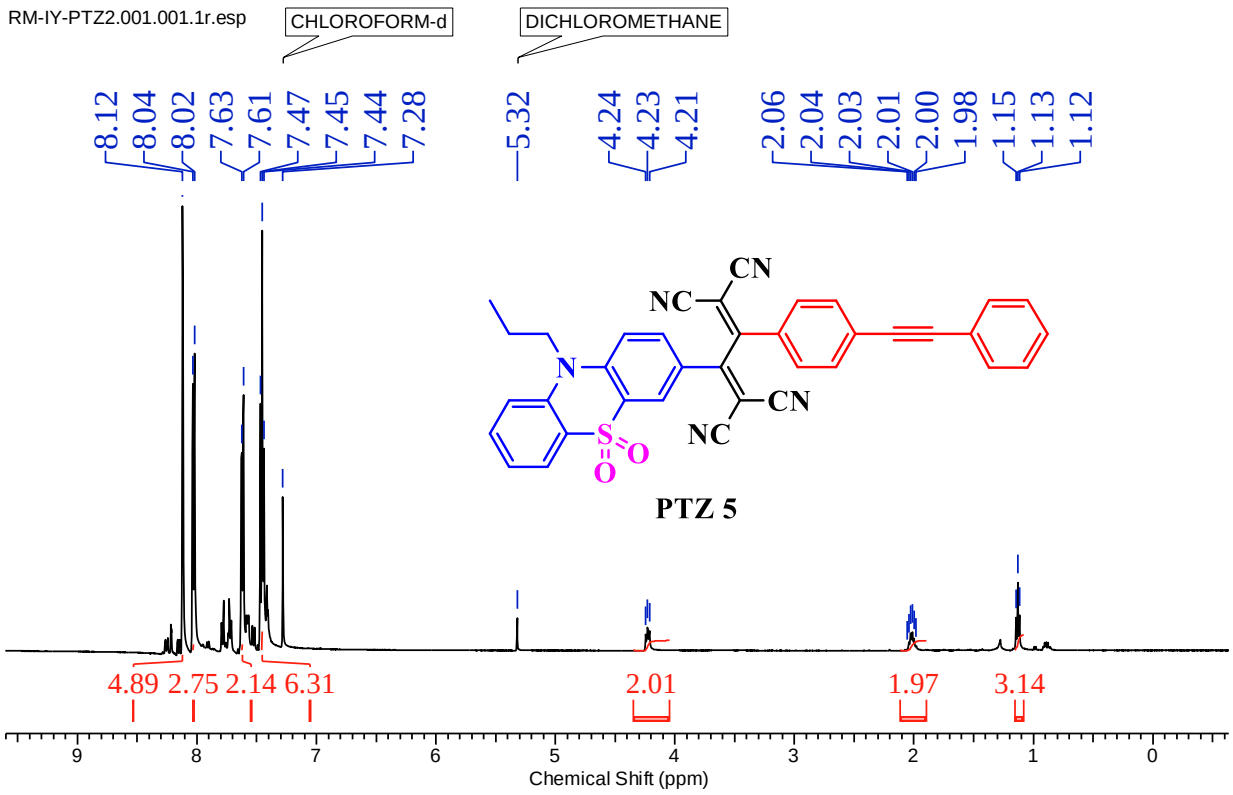


Figure S14. ^{1}H NMR spectrum of **PTZ 5**.

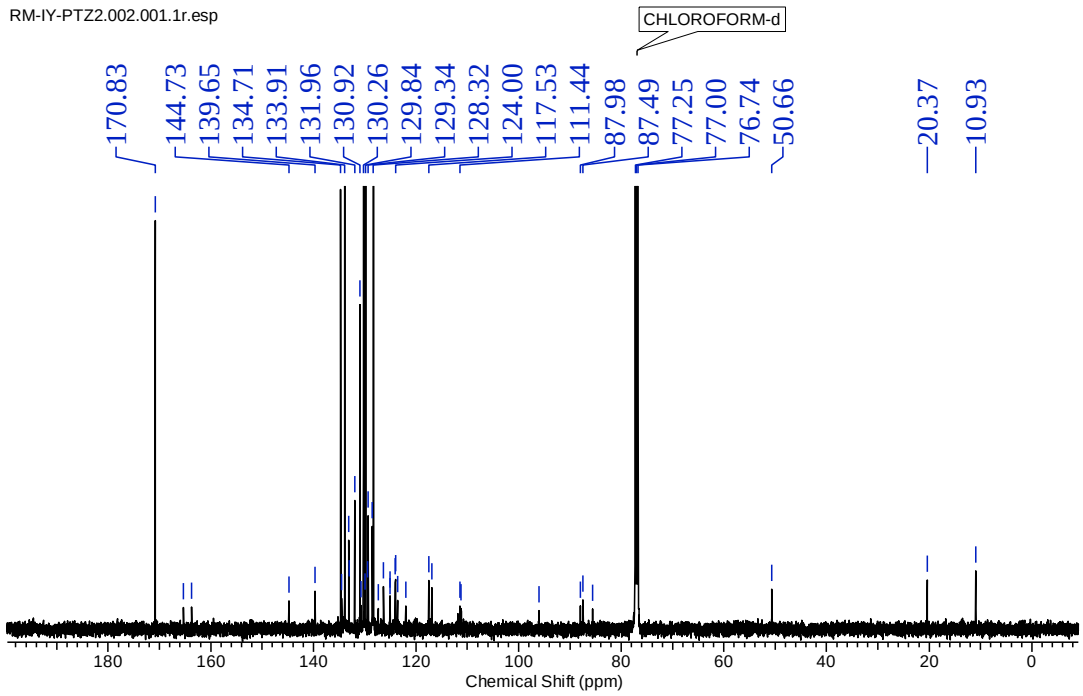


Figure S15. ^{13}C NMR spectrum of **PTZ 5**.

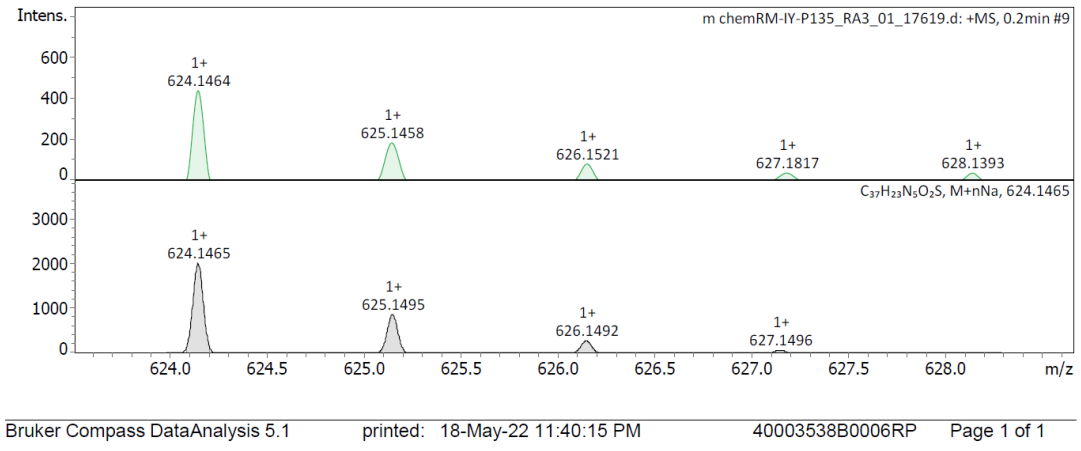


Figure S16. HRMS spectrum of **PTZ 5**.

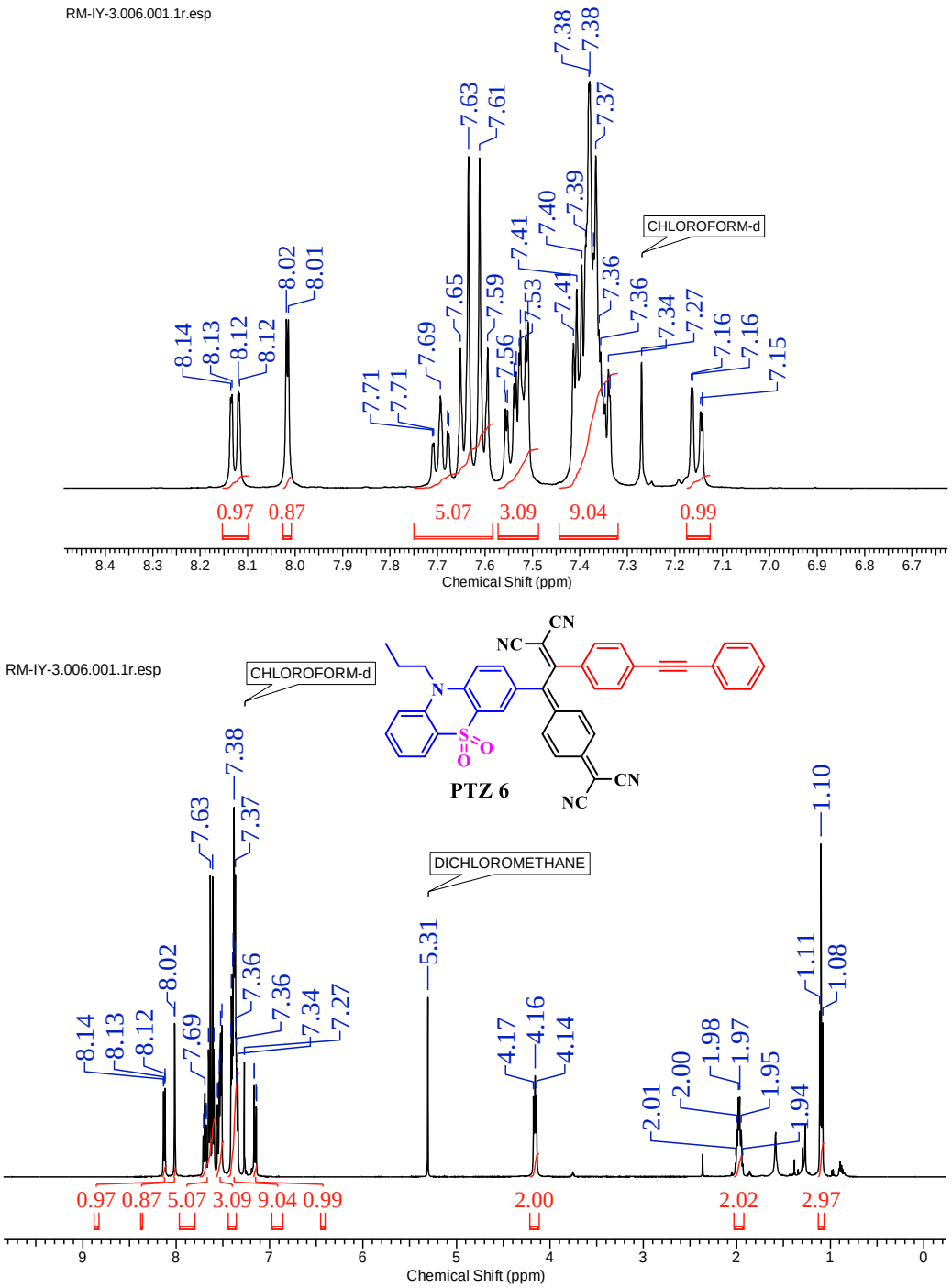


Figure S17. ^{1}H NMR spectrum of **PTZ 6**.

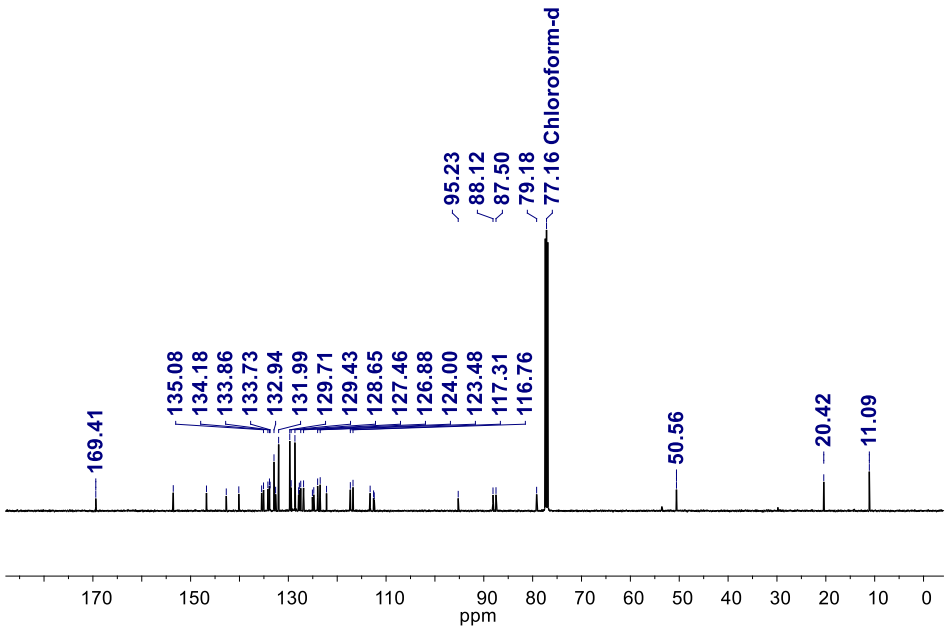


Figure S18. ^{13}C NMR spectrum of **PTZ 6**.

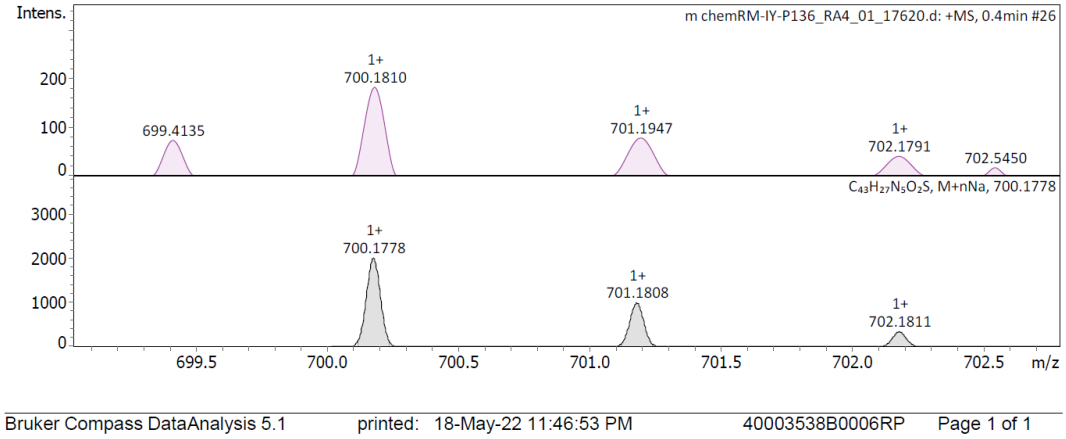


Figure S19. HRMS spectrum of **PTZ 6**.

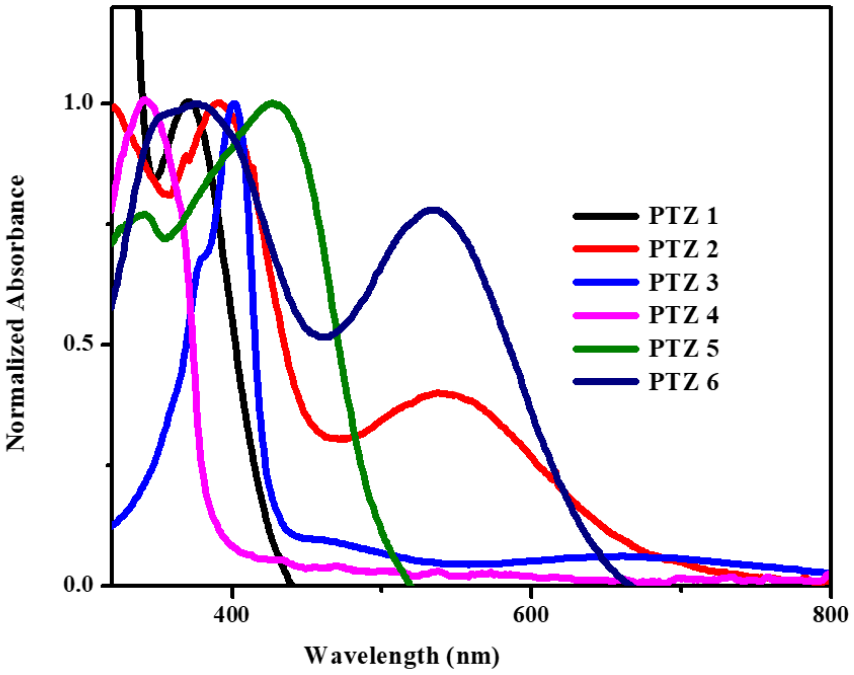
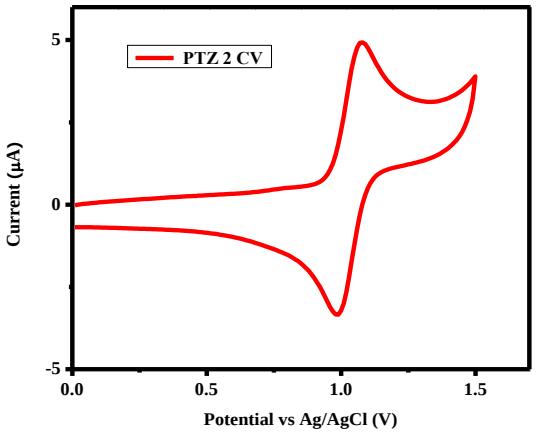
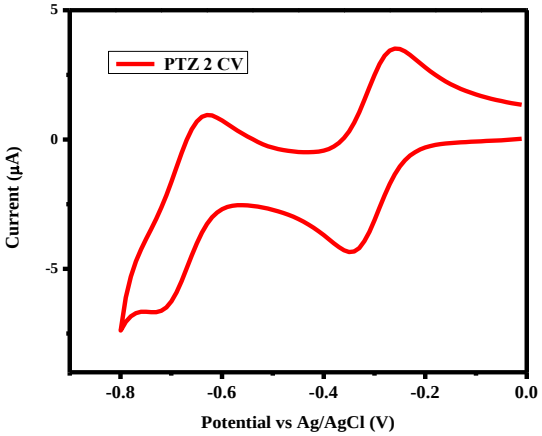
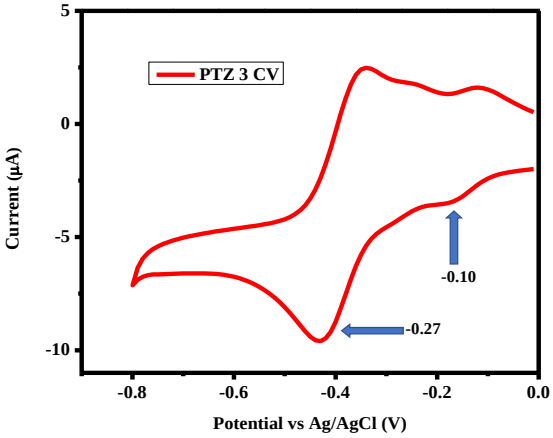


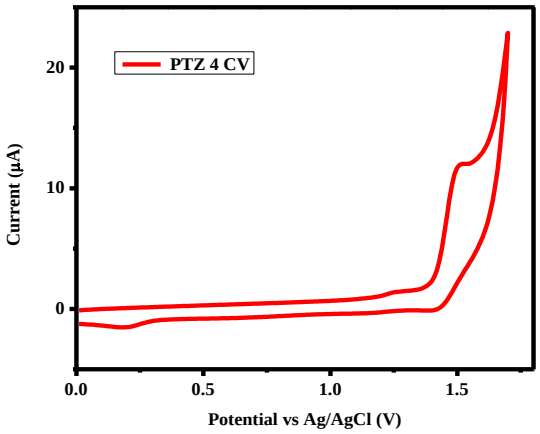
Figure S20. Normalized absorption spectra of push–pull **PTZ 1–6** in dry DCM (1×10^{-5} M)

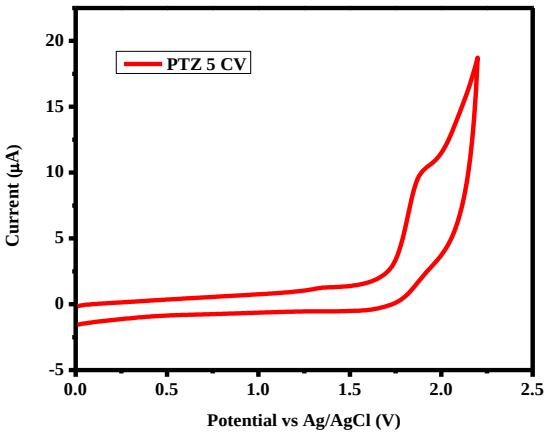
Cyclic Voltammetry:

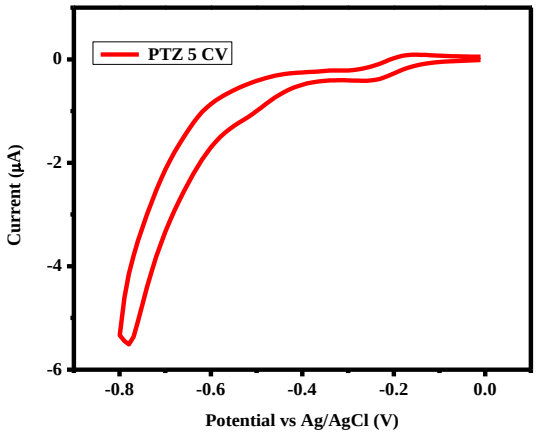




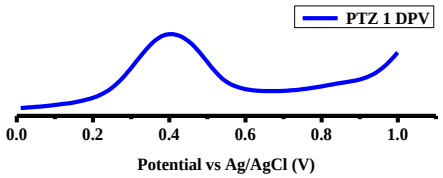


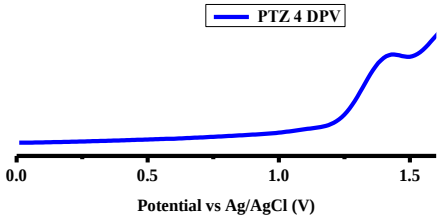


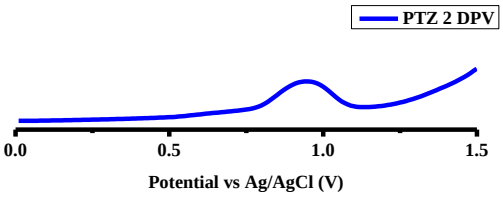


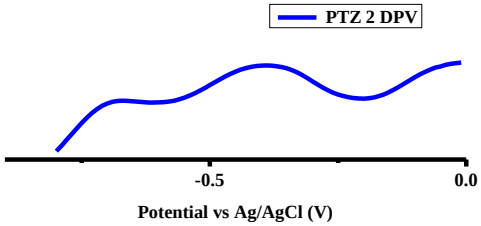


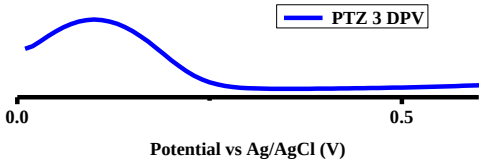
Differential Pulse Voltammetry:

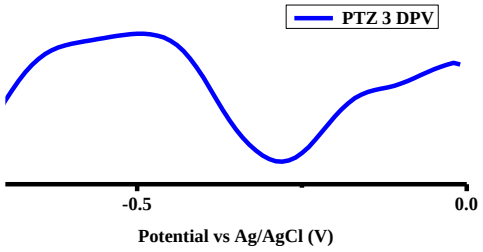


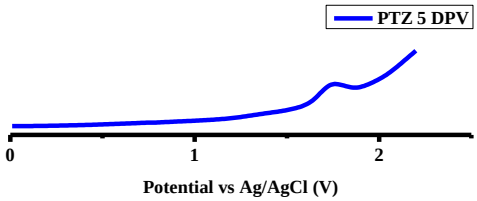


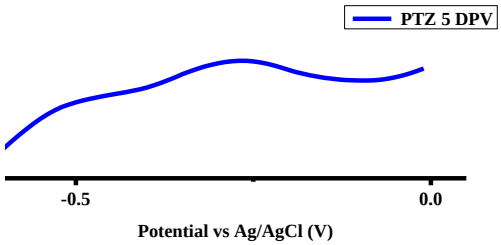


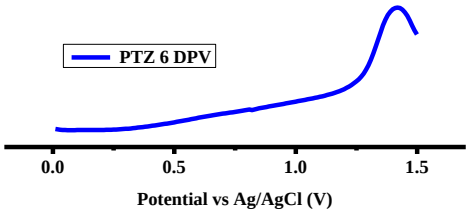



PTZ 3 DPV
0.0
0.5
Potential vs Ag/AgCl (V)


PTZ 3 DPV
-0.5
0.0
Potential vs Ag/AgCl (V)


PTZ 5 DPV
0
1
2
Potential vs Ag/AgCl (V)


PTZ 5 DPV
-0.5
0.0
Potential vs Ag/AgCl (V)


PTZ 6 DPV
0.0
0.5
1.0
1.5
Potential vs Ag/AgCl (V)

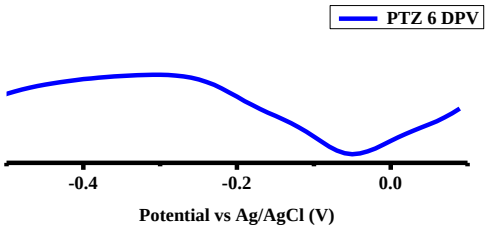

PTZ 6 DPV
-0.4
-0.2
0.0
Potential vs Ag/AgCl (V)

Table S1. The molecular orbital diagram of push–pull **PTZ 1–6**.

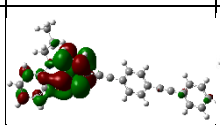
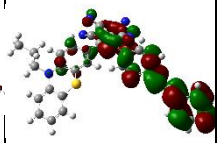
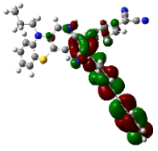
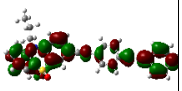
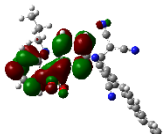
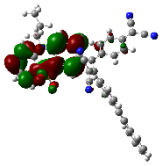
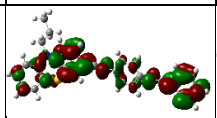
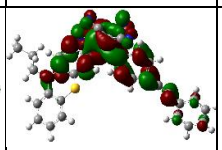
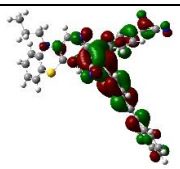
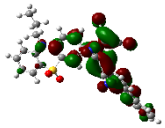
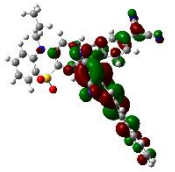
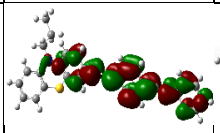
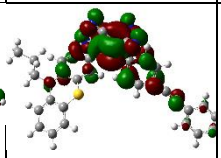
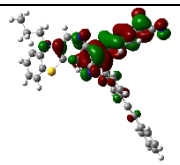
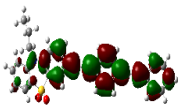
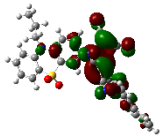
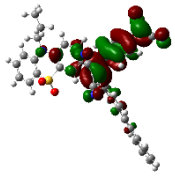
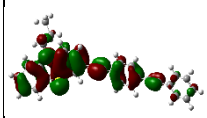
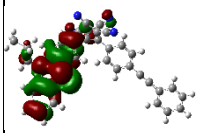
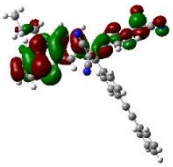
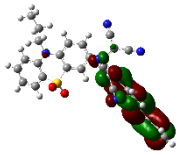
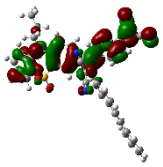
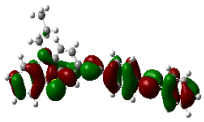
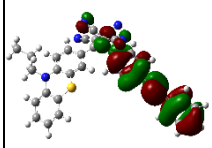
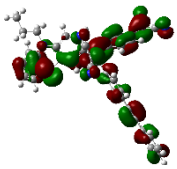
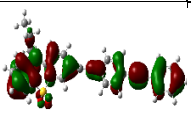
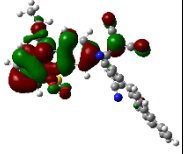
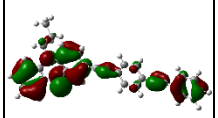
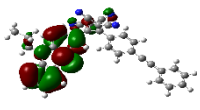
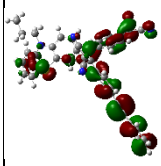
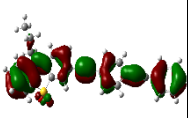
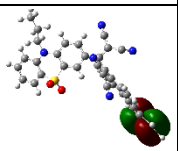
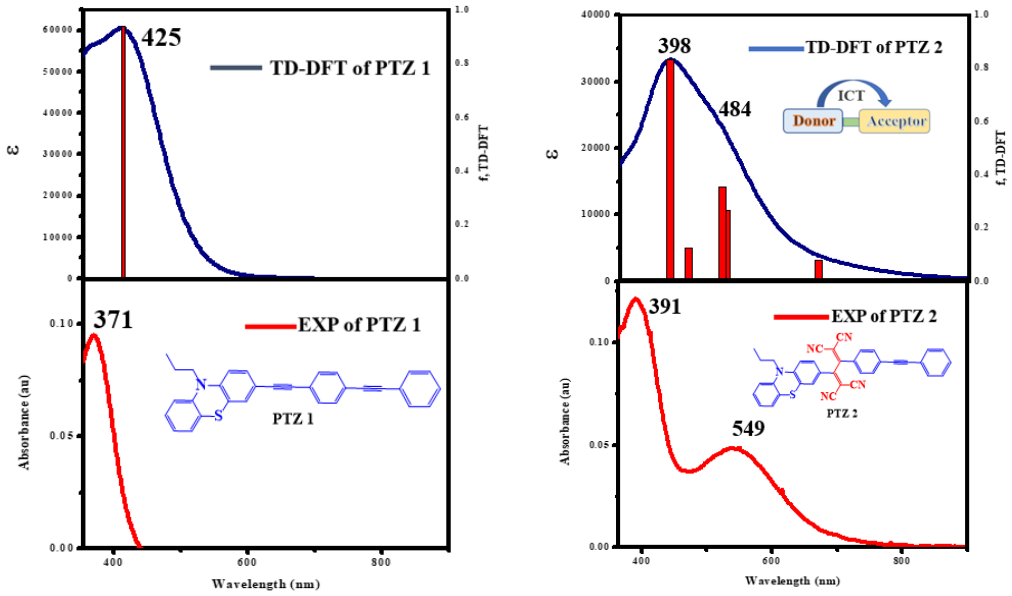
	PTZ 1	PTZ 2	PTZ 3	PTZ 4	PTZ 5	PTZ 6
LUMO+2						
LUMO+1						
LUMO						
HOMO						
HOMO-1						
HOMO-2						

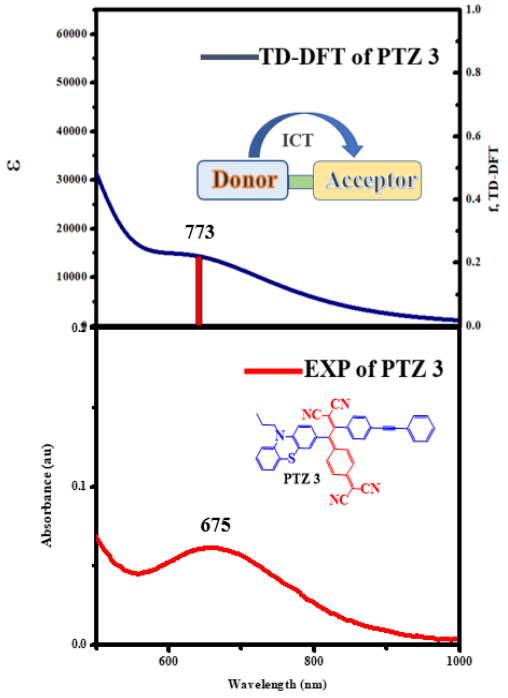
Table S2. Calculated electronic transitions of push–pull **PTZ 1–6**.

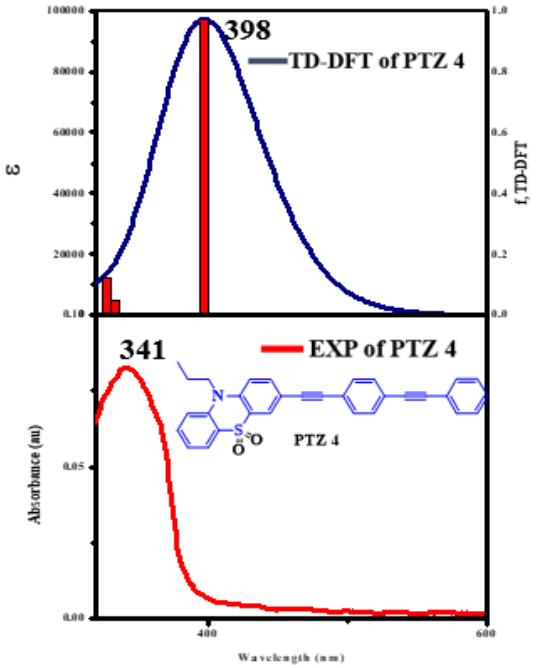
Compounds	Wavelength (nm)	Composition	f[a]	Assignment
PTZ 1	425	HOMO→LUMO (0.69)	1.32	π–π*
PTZ 2	398 484	HOMO-1→LUMO+1 (0.67) HOMO-1→LUMO (0.67)	0.60 0.25	π–π* ICT
PTZ 3	392 773	HOMO-2→LUMO+1 (0.63) HOMO→LUMO (0.67)	0.84 0.22	π–π* ICT
PTZ 4	398	HOMO→LUMO (0.70)	2.38	π–π*
PTZ 5	389 403	HOMO-1→LUMO (0.59) HOMO→LUMO (0.60)	0.54 0.92	π–π* ICT
PTZ 6	404 591	HOMO-1→LUMO+1 (0.61) HOMO→LUMO (0.60)	0.91 0.43	π–π* ICT

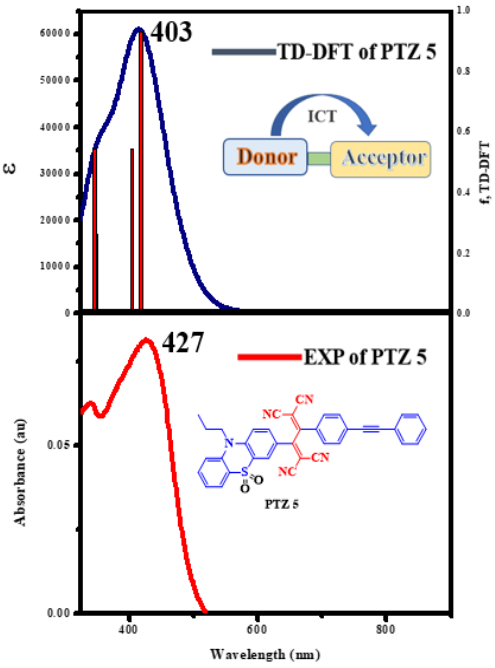
f[a] oscillator strength

Experimental (bottom) and TD-DFT predicted (top) UV-Vis absorption spectra of PTZ 1–5.




TD-DFT of PTZ 3
ICT
Donor
Acceptor
773
EXP of PTZ 3
PTZ 3
675
ε
f, TD-DFT
Absorbance (au)
Wavelength (nm)


398
TD-DFT of PTZ 4
341
EXP of PTZ 4
PTZ 4
ε
f, TD-DFT
Absorbance (au)
Wavelength (nm)


403
TD-DFT of PTZ 5
ICT
Donor
Acceptor
427
EXP of PTZ 5
PTZ 5
ε
f, TD-DFT
Absorbance (au)
Wavelength (nm)

DFT Calculation data

Calculation method: B3LYP/6-31G(d,p) for C, H, N, S and O with Gaussian 09.

PTZ 1.

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.598041	0.425783	-0.058875
2	6	0	2.375914	-0.622236	0.473711
3	6	0	3.762715	-0.539694	0.493249
4	6	0	4.433640	0.572176	-0.058045
5	6	0	3.655330	1.600951	-0.614862
6	6	0	2.267000	1.538461	-0.601505
7	6	0	6.553183	-0.575697	-0.354456
8	6	0	6.118810	-1.801940	0.185178
9	6	0	6.795060	-2.987583	-0.101881
10	1	0	6.429040	-3.919508	0.318016
11	6	0	7.936035	-2.971942	-0.904686
12	6	0	8.367789	-1.766247	-1.453536
13	6	0	7.672474	-0.583089	-1.200778
14	1	0	1.884528	-1.495471	0.889019
15	1	0	4.137202	2.461298	-1.064152
16	1	0	1.687411	2.349907	-1.028439
17	1	0	8.470521	-3.894497	-1.107152

18	1	0	9.239770	-1.740577	-2.100068
19	1	0	8.001073	0.335145	-1.673966
20	6	0	0.178195	0.352955	-0.052659
21	6	0	-9.341805	-0.140026	-0.046944
22	6	0	-10.114305	0.933343	-0.535375
23	6	0	-10.002128	-1.286487	0.439881
24	6	0	-11.503870	0.857756	-0.534706
25	1	0	-9.610766	1.817970	-0.911178
26	6	0	-11.392196	-1.352633	0.436214
27	1	0	-9.412062	-2.115418	0.816784
28	6	0	-12.148075	-0.283134	-0.049983
29	1	0	-11.888230	-2.241829	0.814064
30	7	0	5.844215	0.613175	-0.043043
31	16	0	4.724946	-1.807574	1.297430
32	6	0	-1.037680	0.289692	-0.049239
33	6	0	-2.457032	0.216203	-0.047065
34	6	0	-3.235789	1.277987	-0.554757
35	6	0	-3.121052	-0.920242	0.461999
36	6	0	-4.620263	1.206244	-0.553527
37	1	0	-2.736701	2.157054	-0.948790
38	6	0	-4.505587	-0.991891	0.462746
39	1	0	-2.533230	-1.743111	0.854973
40	6	0	-5.284019	0.069706	-0.045048
41	1	0	-5.208248	2.028986	-0.946636
42	1	0	-5.004716	-1.871075	0.856479
43	6	0	-6.703978	-0.004053	-0.044988
44	6	0	-7.919464	-0.067107	-0.045622

45	6	0	6.528079	1.906034	-0.140407
46	1	0	7.599570	1.699395	-0.133592
47	1	0	6.315621	2.410939	-1.096222
48	1	0	-12.086994	1.691898	-0.913762
49	1	0	-13.232545	-0.338437	-0.051151
50	6	0	6.219192	2.838734	1.039325
51	1	0	5.143365	3.029798	1.101015
52	1	0	6.495842	2.321559	1.964976
53	6	0	6.974421	4.166133	0.925129
54	1	0	6.695777	4.709992	0.015200
55	1	0	6.754364	4.815314	1.777553
56	1	0	8.058960	4.010673	0.898523

Total Energy (HF) =-1648.0376056 Hartrees

PTZ 2. Calculation method: B3LYP/6-31G(d,p)

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z

1	6	0	4.283192	5.431746	0.223535
2	6	0	3.481824	4.492072	0.871349
3	6	0	3.739527	3.128362	0.728390
4	6	0	4.789736	2.676639	-0.091227
5	6	0	5.554072	3.631357	-0.778539

6	6	0	5.315116	4.994621	-0.604376
7	6	0	3.944250	0.412098	-0.346043
8	6	0	2.772488	0.639951	0.414283
9	6	0	1.677138	-0.200740	0.297377
10	1	0	0.796762	0.014875	0.893093
11	6	0	2.873843	-1.559422	-1.297455
12	6	0	3.965281	-0.712481	-1.194151
13	1	0	4.091464	6.491625	0.355121
14	1	0	2.657560	4.810886	1.501791
15	1	0	6.333023	3.315170	-1.462523
16	1	0	5.931363	5.712447	-1.136678
17	1	0	2.955452	-2.425295	-1.940702
18	1	0	4.849089	-0.933334	-1.779194
19	6	0	-1.714174	-1.604116	0.435479
20	6	0	-1.880902	-0.513987	-0.447832
21	6	0	-2.840988	-2.049942	1.159161
22	6	0	-3.100780	0.129769	-0.570266
23	1	0	-1.038517	-0.157272	-1.030780
24	6	0	-4.066177	-1.418655	1.026409
25	1	0	-2.769022	-2.917103	1.802608
26	6	0	-4.220575	-0.309179	0.167422
27	1	0	-3.205160	0.975341	-1.241042
28	1	0	-4.924816	-1.784835	1.578008
29	6	0	-5.475163	0.340096	0.038050
30	6	0	-7.811317	1.547633	-0.200403
31	6	0	-8.927748	1.093154	0.530571
32	6	0	-7.959796	2.654760	-1.060325

33	6	0	-10.156813	1.732250	0.401479
34	1	0	-8.815616	0.240837	1.192413
35	6	0	-9.193242	3.286762	-1.182071
36	1	0	-7.101930	3.005586	-1.624352
37	6	0	-10.293822	2.828917	-0.453265
38	1	0	-9.297496	4.138601	-1.847237
39	6	0	-0.396987	-2.241262	0.552122
40	7	0	5.031290	1.281461	-0.233216
41	16	0	2.772897	1.936788	1.634781
42	6	0	-6.551811	0.897386	-0.072123
43	6	0	1.693307	-1.320826	-0.565450
44	6	0	0.517746	-2.187078	-0.645938
45	6	0	6.377886	0.811944	-0.594420
46	1	0	6.432976	0.534474	-1.657106
47	1	0	7.054111	1.656209	-0.459145
48	6	0	0.157644	-2.956152	-1.731651
49	6	0	-0.963281	-3.846939	-1.668424
50	6	0	0.825765	-2.936808	-2.997105
51	7	0	-1.866008	-4.580899	-1.632842
52	7	0	1.328895	-2.939152	-4.046977
53	6	0	0.083487	-2.873154	1.675160
54	6	0	-0.592230	-2.914755	2.937602
55	6	0	1.354015	-3.538913	1.666353
56	7	0	-1.091357	-2.960770	3.987962
57	7	0	2.379013	-4.089622	1.681122
58	1	0	-11.254839	3.324688	-0.551365
59	1	0	-11.010760	1.374372	0.968557

60	6	0	6.870259	-0.337934	0.296106
61	1	0	6.849135	0.002586	1.337369
62	1	0	6.186278	-1.190167	0.235387
63	6	0	8.284171	-0.782797	-0.089694
64	1	0	8.627531	-1.591612	0.561187
65	1	0	8.322134	-1.150353	-1.121373
66	1	0	9.002446	0.040269	-0.003419

Total Energy (HF) =-2095.6229188 Hartrees

PTZ 3. Calculation method: B3LYP/6-31G(d,p)

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-5.671132	-4.382071	-2.827293
2	6	0	-4.675260	-4.229945	-1.862970
3	6	0	-4.645230	-3.092474	-1.055571
4	6	0	-5.591950	-2.066141	-1.223103
5	6	0	-6.567201	-2.216461	-2.220201
6	6	0	-6.614326	-3.370921	-3.001492
7	6	0	-4.277414	-0.345615	-0.118144
8	6	0	-3.177572	-1.193933	0.158469
9	6	0	-1.929771	-0.667692	0.456063
10	1	0	-1.112397	-1.353282	0.655441

11	6	0	-2.809645	1.565160	0.244648
12	6	0	-4.055689	1.044097	-0.072025
13	1	0	-5.702687	-5.278182	-3.438391
14	1	0	-3.921878	-4.998702	-1.721898
15	1	0	-7.295096	-1.431812	-2.389835
16	1	0	-7.387598	-3.468180	-3.757177
17	1	0	-2.697392	2.639818	0.327956
18	1	0	-4.866523	1.731241	-0.280342
19	6	0	1.696181	-0.083575	1.458465
20	6	0	1.886010	-0.474842	0.115024
21	6	0	2.771579	-0.259188	2.355531
22	6	0	3.076185	-1.044220	-0.307235
23	1	0	1.081309	-0.342711	-0.599906
24	6	0	3.970175	-0.811516	1.933444
25	1	0	2.681961	0.063308	3.385424
26	6	0	4.145911	-1.223808	0.594994
27	1	0	3.196153	-1.352540	-1.339980
28	1	0	4.790216	-0.923983	2.634015
29	6	0	5.372133	-1.792550	0.163723
30	6	0	7.653917	-2.846387	-0.646171
31	6	0	8.714291	-3.041245	0.261990
32	6	0	7.828830	-3.219649	-1.994233
33	6	0	9.914889	-3.594670	-0.171642
34	1	0	8.581858	-2.754517	1.299930
35	6	0	9.033562	-3.771890	-2.417607
36	1	0	7.014078	-3.069913	-2.694874
37	6	0	10.078710	-3.961004	-1.509910

38	1	0	9.158650	-4.055463	-3.458201
39	6	0	0.404878	0.496964	1.865354
40	7	0	-5.528690	-0.900202	-0.412560
41	16	0	-3.439625	-2.952515	0.249013
42	6	0	6.423877	-2.279110	-0.208936
43	6	0	-1.706495	0.726630	0.503198
44	6	0	-6.752202	-0.115218	-0.193348
45	1	0	-6.484189	0.723871	0.449485
46	1	0	-7.126086	0.316087	-1.133716
47	6	0	1.845627	5.925806	-1.487651
48	6	0	2.977649	6.574320	-0.916107
49	6	0	1.294425	6.508056	-2.664952
50	7	0	3.904946	7.091545	-0.434662
51	7	0	0.828559	6.967831	-3.629780
52	6	0	-0.139745	0.339778	3.123475
53	6	0	0.402362	-0.506466	4.144140
54	6	0	-1.331798	1.032464	3.517447
55	7	0	0.795321	-1.189204	5.001432
56	7	0	-2.284442	1.595979	3.877498
57	6	0	-0.381023	1.255506	0.839703
58	6	0	0.174801	2.389967	0.245533
59	6	0	-0.362243	2.981717	-0.961389
60	6	0	1.336104	3.046711	0.806706
61	6	0	0.172914	4.100533	-1.518103
62	1	0	-1.182654	2.484843	-1.464628
63	6	0	1.861134	4.177850	0.266748
64	1	0	1.776398	2.647441	1.712860

65	6	0	1.302143	4.769258	-0.922833
66	1	0	-0.234078	4.493908	-2.443742
67	1	0	2.713417	4.658654	0.735156
68	1	0	11.017518	-4.391996	-1.844276
69	1	0	10.725793	-3.740509	0.535484
70	6	0	-7.856813	-0.913353	0.513344
71	1	0	-8.127285	-1.793875	-0.077313
72	1	0	-7.456459	-1.285369	1.462985
73	6	0	-9.100268	-0.053981	0.761002
74	1	0	-9.528849	0.313093	-0.178459
75	1	0	-9.874941	-0.631207	1.273521
76	1	0	-8.870155	0.817234	1.384275

Total Energy (HF) =-2326.6698198 Hartrees

PTZ 4. Calculation method: B3LYP/6-31G(d,p)

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.242092	0.573794	0.285135
2	6	0	2.037028	-0.581649	0.289631
3	6	0	3.423413	-0.484482	0.331965
4	6	0	4.102099	0.754573	0.322852
5	6	0	3.287750	1.908911	0.351994
6	6	0	1.905320	1.818132	0.340320

7	6	0	6.296505	-0.216344	-0.223728
8	6	0	5.832218	-1.548739	-0.256936
9	6	0	6.578689	-2.585687	-0.819032
10	1	0	6.148903	-3.581890	-0.830964
11	6	0	7.844987	-2.333243	-1.329952
12	6	0	8.348472	-1.031891	-1.260336
13	6	0	7.594650	0.009164	-0.728936
14	1	0	1.582401	-1.565997	0.275038
15	1	0	3.732321	2.894362	0.358740
16	1	0	1.315498	2.728572	0.352796
17	1	0	8.433873	-3.133769	-1.764255
18	1	0	9.340549	-0.812969	-1.643838
19	1	0	8.017535	1.004139	-0.732825
20	6	0	-0.175726	0.494400	0.236982
21	6	0	-9.680100	-0.080768	-0.168982
22	6	0	-10.468761	1.086955	-0.209985
23	6	0	-10.321126	-1.336039	-0.194834
24	6	0	-11.855893	0.997010	-0.275292
25	1	0	-9.979645	2.055312	-0.190228
26	6	0	-11.708949	-1.415558	-0.260080
27	1	0	-9.718259	-2.237637	-0.163255
28	6	0	-12.481081	-0.252043	-0.300571
29	1	0	-12.190527	-2.388766	-0.279372
30	7	0	5.500110	0.840749	0.254466
31	16	0	4.346915	-1.971553	0.608972
32	6	0	-1.390111	0.426998	0.191402
33	6	0	-2.807853	0.341238	0.134677

34	6	0	-3.601223	1.507622	0.108584
35	6	0	-3.452411	-0.913510	0.100946
36	6	0	-4.983708	1.422992	0.049493
37	1	0	-3.115949	2.477654	0.134667
38	6	0	-4.834947	-0.997572	0.042104
39	1	0	-2.851945	-1.816815	0.121342
40	6	0	-5.628833	0.168607	0.014539
41	1	0	-5.584288	2.326282	0.029229
42	1	0	-5.320324	-1.967445	0.016238
43	6	0	-7.046577	0.081738	-0.048187
44	6	0	-8.260063	0.006527	-0.103296
45	6	0	6.144270	2.131208	0.550566
46	1	0	5.579601	2.598955	1.361984
47	1	0	7.132054	1.913148	0.965940
48	1	0	-12.451917	1.904327	-0.306581
49	1	0	-13.563732	-0.318368	-0.351437
50	6	0	6.274393	3.107213	-0.632169
51	1	0	6.826226	2.629804	-1.448421
52	1	0	5.283308	3.333363	-1.038841
53	6	0	6.976231	4.402706	-0.212803
54	1	0	7.063102	5.092408	-1.056985
55	1	0	6.424983	4.918286	0.581649
56	1	0	7.987341	4.207036	0.161646
57	8	0	4.654536	-2.063275	2.047136
58	8	0	3.684585	-3.108470	-0.051326

Total Energy (HF) =-1798.417541 Hartrees

PTZ 5. Calculation method: B3LYP/6-31G(d,p)

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-4.556916	-5.072976	0.480142
2	6	0	-3.605202	-4.184655	0.963579
3	6	0	-3.763664	-2.812919	0.758961
4	6	0	-4.848380	-2.279951	0.032081
5	6	0	-5.809368	-3.200767	-0.432722
6	6	0	-5.664512	-4.565021	-0.202343
7	6	0	-3.857033	-0.047834	-0.238016
8	6	0	-2.661696	-0.371831	0.446591
9	6	0	-1.527465	0.424236	0.381765
10	1	0	-0.647505	0.093541	0.923802
11	6	0	-2.734612	1.988850	-0.982886
12	6	0	-3.862179	1.192636	-0.921059
13	1	0	-4.444619	-6.139877	0.638870
14	1	0	-2.735303	-4.527866	1.513703
15	1	0	-6.666583	-2.863287	-0.998170
16	1	0	-6.424986	-5.240665	-0.581626
17	1	0	-2.806480	2.930868	-1.510745
18	1	0	-4.751793	1.538370	-1.427807
19	6	0	1.938154	1.667879	0.508109
20	6	0	2.018223	0.629772	-0.447578

21	6	0	3.109611	2.003615	1.221135
22	6	0	3.196520	-0.066802	-0.654280
23	1	0	1.140248	0.353432	-1.021540
24	6	0	4.293594	1.319528	1.005064
25	1	0	3.105570	2.826376	1.923808
26	6	0	4.361373	0.264150	0.069819
27	1	0	3.232599	-0.871874	-1.379636
28	1	0	5.187200	1.601995	1.550270
29	6	0	5.574673	-0.436996	-0.148214
30	6	0	7.833802	-1.740700	-0.559034
31	6	0	8.991087	-1.413917	0.176637
32	6	0	7.899756	-2.771839	-1.518097
33	6	0	10.179365	-2.102851	-0.044773
34	1	0	8.942425	-0.620739	0.915238
35	6	0	9.093115	-3.454269	-1.731967
36	1	0	7.010118	-3.024606	-2.085351
37	6	0	10.234745	-3.123089	-0.997743
38	1	0	9.133768	-4.246678	-2.473161
39	6	0	0.663480	2.365455	0.707991
40	7	0	-4.955352	-0.901557	-0.259262
41	16	0	-2.659284	-1.717476	1.603364
42	6	0	6.615897	-1.038691	-0.337377
43	6	0	-1.520293	1.612154	-0.366946
44	6	0	-0.297684	2.416636	-0.452586
45	6	0	-6.248014	-0.384788	-0.750934
46	1	0	-6.341047	0.647378	-0.403516
47	1	0	-7.034113	-0.940477	-0.233867

48	6	0	0.046362	3.211567	-1.520570
49	6	0	1.216390	4.039575	-1.487151
50	6	0	-0.693177	3.276285	-2.745644
51	7	0	2.156620	4.725016	-1.478600
52	7	0	-1.258340	3.341399	-3.761024
53	6	0	0.255159	2.976727	1.871157
54	6	0	0.976795	2.946936	3.107606
55	6	0	-0.976272	3.710340	1.922420
56	7	0	1.519681	2.945128	4.136966
57	7	0	-1.968873	4.315922	1.970250
58	1	0	11.164201	-3.658065	-1.167628
59	1	0	11.065266	-1.843747	0.526984
60	6	0	-6.457096	-0.455103	-2.273060
61	1	0	-5.666540	0.105373	-2.782698
62	1	0	-6.353205	-1.490314	-2.614102
63	6	0	-7.829862	0.094760	-2.673474
64	1	0	-7.969411	0.043421	-3.756621
65	1	0	-8.641513	-0.473944	-2.206189
66	1	0	-7.945107	1.142197	-2.373697
67	8	0	-3.308000	-1.259647	2.842320
68	8	0	-1.313109	-2.307748	1.671670

Total Energy (HF) =-2246.0003846 Hartrees

PTZ 6. Calculation method: B3LYP/6-31G(d,p)

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-5.614881	-4.688490	-2.277265
2	6	0	-4.513704	-4.378560	-1.490075
3	6	0	-4.458627	-3.157298	-0.816115
4	6	0	-5.473329	-2.184594	-0.934526
5	6	0	-6.589036	-2.531461	-1.723973
6	6	0	-6.655215	-3.761247	-2.370807
7	6	0	-4.145007	-0.365406	0.050175
8	6	0	-2.994339	-1.161473	0.258943
9	6	0	-1.751558	-0.615255	0.549645
10	1	0	-0.916423	-1.296343	0.679437
11	6	0	-2.737618	1.570380	0.531970
12	6	0	-3.975569	1.027114	0.238013
13	1	0	-5.668284	-5.636995	-2.800285
14	1	0	-3.687689	-5.071840	-1.370711
15	1	0	-7.405407	-1.835983	-1.859515
16	1	0	-7.530212	-3.986204	-2.972907
17	1	0	-2.667644	2.639199	0.699083
18	1	0	-4.817002	1.700025	0.151650
19	6	0	1.865750	0.025932	1.461030
20	6	0	1.994761	-0.343649	0.103875
21	6	0	2.982866	-0.159954	2.304423
22	6	0	3.165440	-0.901899	-0.382195
23	1	0	1.157774	-0.206225	-0.571869

24	6	0	4.161707	-0.700673	1.818088
25	1	0	2.941192	0.143978	3.342694
26	6	0	4.276449	-1.091440	0.466447
27	1	0	3.236867	-1.195739	-1.423517
28	1	0	5.013373	-0.821983	2.478236
29	6	0	5.483433	-1.648579	-0.028342
30	6	0	7.733030	-2.682255	-0.946646
31	6	0	8.833568	-2.875139	-0.087063
32	6	0	7.850329	-3.047703	-2.303055
33	6	0	10.017093	-3.419011	-0.576051
34	1	0	8.745111	-2.594879	0.957299
35	6	0	9.038441	-3.590529	-2.781907
36	1	0	7.004284	-2.900254	-2.966050
37	6	0	10.123713	-3.777734	-1.922139
38	1	0	9.119037	-3.868706	-3.828330
39	6	0	0.595401	0.596760	1.936098
40	7	0	-5.368848	-0.911857	-0.333462
41	16	0	-3.161328	-2.924944	0.365702
42	6	0	6.520310	-2.125480	-0.451820
43	6	0	-1.578174	0.773324	0.660204
44	6	0	-6.579264	-0.072511	-0.245548
45	1	0	-6.486848	0.539954	0.655284
46	1	0	-7.423145	-0.741587	-0.059795
47	6	0	1.678925	6.144947	-1.355328
48	6	0	2.832815	6.806175	-0.843511
49	6	0	1.028996	6.751707	-2.469011
50	7	0	3.778481	7.334012	-0.412655

51	7	0	0.482655	7.230589	-3.380544
52	6	0	0.117623	0.461113	3.223345
53	6	0	0.719429	-0.348420	4.239746
54	6	0	-1.057666	1.161288	3.652916
55	7	0	1.168207	-0.993060	5.098911
56	7	0	-1.995547	1.741594	4.025003
57	6	0	-0.255189	1.345315	0.952307
58	6	0	0.224900	2.512017	0.365607
59	6	0	-0.414479	3.131227	-0.778410
60	6	0	1.408903	3.181067	0.866871
61	6	0	0.051821	4.280600	-1.331301
62	1	0	-1.260435	2.632893	-1.235835
63	6	0	1.866445	4.341264	0.330388
64	1	0	1.923193	2.760398	1.722720
65	6	0	1.207666	4.957280	-0.795441
66	1	0	-0.432574	4.697513	-2.208030
67	1	0	2.739561	4.828514	0.751204
68	1	0	11.049230	-4.201701	-2.299769
69	1	0	10.859135	-3.563705	0.093930
70	8	0	-3.677674	-3.258534	1.702871
71	8	0	-1.924976	-3.567964	-0.107624
72	6	0	-6.864853	0.817626	-1.466742
73	1	0	-6.946993	0.198896	-2.366335
74	1	0	-6.016895	1.487499	-1.644457
75	6	0	-8.145883	1.635519	-1.273582
76	1	0	-9.017521	0.986885	-1.131938
77	1	0	-8.075467	2.289541	-0.397424

78 1 0 -8.340948 2.267591 -2.144171

Total Energy (HF) =-2477.0471742 Hartrees

TD-DFT Calculation data

Calculation method: B3LYP/6-31G(d,p) and CAM-B3LYP/6-31G(d,p) level in dichloromethane solvent/ gas phase.

TD-DFT of PTZ 1 in DCM solvent. Calculation method: B3LYP/6-31G(d,p)

Excitation energies and oscillator strengths:

Excited State 1: Singlet-A 2.9125 eV 425.69 nm f=1.3216
<S**2>=0.000
116 ->117 0.69773
This state for optimization and/or second-order correction.
Total Energy, E(TD-HF/TD-KS) = -1647.93945641
Copying the excited state density for this state as the 1-particle RhoCI density.

Excited State 2: Singlet-A 3.5073 eV 353.50 nm f=1.1583
<S**2>=0.000
115 ->117 0.69505

Excited State 3: Singlet-A 3.7968 eV 326.55 nm f=0.0031
<S**2>=0.000
116 ->118 0.55801
116 ->119 0.32969
116 ->120 0.18371

Excited State 4: Singlet-A 3.9474 eV 314.09 nm f=0.0290
<S**2>=0.000
114 ->117 0.46513
116 ->118 -0.26610
116 ->119 0.42088

Excited State 5: Singlet-A 4.1333 eV 299.96 nm f=0.0269
<S**2>=0.000
114 ->117 0.43616
116 ->118 0.11148
116 ->119 -0.40278
116 ->120 0.32185

Excited State 6: Singlet-A 4.1994 eV 295.24 nm f=0.0764
<S**2>=0.000
114 ->117 -0.27536
116 ->118 -0.22503
116 ->119 0.12022
116 ->120 0.55979
116 ->123 0.13370

Excited State 7: Singlet-A 4.3233 eV 286.78 nm f=0.0011
<S**2>=0.000
110 ->117 0.33805
115 ->121 0.22268
116 ->121 0.57342

Excited State 8: Singlet-A 4.3710 eV 283.65 nm f=0.0026
<S**2>=0.000
113 ->117 0.60389
115 ->118 -0.23348
116 ->123 -0.23593

Excited State 9: Singlet-A 4.5319 eV 273.58 nm f=0.0087
<S**2>=0.000
113 ->117 0.32998
114 ->118 -0.10324
115 ->118 0.47921
116 ->118 0.17036
116 ->123 0.26541

Excited State 10: Singlet-A 4.5531 eV 272.31 nm f=0.0002
<S**2>=0.000
112 ->117 0.45109
112 ->118 0.12487
115 ->122 0.26567

116 ->122 0.43512

TD-DFT of PTZ 2 in gas phase. Calculation method: B3LYP/6-31G(d,p)

Excitation energies and oscillator strengths:

Excited State 1: Singlet-A 1.9323 eV 641.64 nm f=0.0600
<S**2>=0.000
148 ->149 0.70132
This state for optimization and/or second-order correction.
Total Energy, E(TD-HF/TD-KS) = -2095.55190839
Copying the excited state density for this state as the 1-particle RhoCI density.

Excited State 2: Singlet-A 2.5287 eV 490.30 nm f=0.1934
<S**2>=0.000
146 ->149 0.13433
147 ->149 0.11035
148 ->150 0.67452

Excited State 3: Singlet-A 2.5565 eV 484.98 nm f=0.2569
<S**2>=0.000
147 ->149 0.67970
147 ->150 0.15010

Excited State 4: Singlet-A 2.8935 eV 428.49 nm f=0.0920
<S**2>=0.000
146 ->149 0.68240
148 ->150 -0.13071

Excited State 5: Singlet-A 3.1089 eV 398.80 nm f=0.6022
<S**2>=0.000
147 ->149 -0.14801
147 ->150 0.67631

Excited State 6: Singlet-A 3.3608 eV 368.91 nm f=0.0205
<S**2>=0.000
143 ->149 0.10793
145 ->149 0.56524
146 ->150 -0.38050

Excited State 7: Singlet-A 3.5087 eV 353.36 nm f=0.1639
<S**2>=0.000
145 ->149 0.36242
146 ->150 0.57118
148 ->152 0.11418

Excited State 8: Singlet-A 3.6469 eV 339.97 nm f=0.0014
<S**2>=0.000
144 ->149 0.70167

Excited State 9: Singlet-A 3.6615 eV 338.62 nm f=0.0150
<S**2>=0.000
141 ->149 0.49716
142 ->149 -0.39358
143 ->149 -0.27014

Excited State 10: Singlet-A 3.7090 eV 334.28 nm f=0.0426
<S**2>=0.000
142 ->149 -0.38546
143 ->149 0.53112
143 ->150 0.11864
148 ->151 -0.10424
148 ->152 -0.12052

Excited State 11: Singlet-A 3.7986 eV 326.40 nm f=0.0542
<S**2>=0.000
140 ->149 -0.15840
141 ->149 0.31644
142 ->149 0.22334
143 ->149 0.24061
145 ->150 -0.11878
148 ->151 0.32799
148 ->152 0.29750
148 ->154 -0.11899

Excited State 12: Singlet-A 3.8089 eV 325.52 nm f=0.0060
<S**2>=0.000
140 ->149 0.62099
140 ->150 -0.18216

148 ->151 0.19503
148 ->152 0.12862

Excited State 13: Singlet-A 3.8257 eV 324.08 nm f=0.0299
<S**2>=0.000
140 ->149 -0.18749
141 ->149 -0.32598
142 ->149 -0.32922
145 ->150 0.13337
148 ->151 0.38758
148 ->152 0.16808
148 ->154 -0.13210

Excited State 14: Singlet-A 3.9562 eV 313.39 nm f=0.0716
<S**2>=0.000
145 ->150 0.10277
146 ->150 -0.10320
148 ->151 -0.41288
148 ->152 0.51799

Excited State 15: Singlet-A 4.0138 eV 308.89 nm f=0.1551
<S**2>=0.000
139 ->149 -0.20533
141 ->149 0.13297
143 ->149 0.11980
145 ->150 0.61006

TD-DFT of PTZ 3 in gas phase. Calculation method: B3LYP/6-31G(d,p)

Excitation energies and oscillator strengths:

Excited State 1: Singlet-A 1.6026 eV 773.62 nm f=0.2219
<S**2>=0.000
167 ->169 0.17017
168 ->169 0.67460
168 ->170 0.10295
This state for optimization and/or second-order correction.
Total Energy, E(TD-HF/TD-KS) = -2326.61092378
Copying the excited state density for this state as the 1-particle RhoCI density.

Excited State 2: Singlet-A 2.1552 eV 575.28 nm f=0.1193
<S**2>=0.000
166 ->169 0.57619
167 ->169 0.39641

Excited State 3: Singlet-A 2.2156 eV 559.59 nm f=0.0705
<S**2>=0.000
165 ->169 -0.10629
166 ->169 0.24528
167 ->169 -0.39336
168 ->170 0.50677

Excited State 4: Singlet-A 2.4562 eV 504.79 nm f=0.5400
<S**2>=0.000
165 ->169 0.29692
166 ->169 -0.25335
166 ->170 -0.10510
167 ->169 0.29282
168 ->169 -0.18540
168 ->170 0.45750

Excited State 5: Singlet-A 2.6357 eV 470.40 nm f=0.1273
<S**2>=0.000
165 ->169 0.60516
166 ->169 0.10492
166 ->170 0.19409
167 ->169 -0.18400
167 ->170 -0.16486
168 ->170 -0.12162

Excited State 6: Singlet-A 2.9429 eV 421.31 nm f=0.3088
<S**2>=0.000
162 ->169 -0.11093
163 ->169 0.14942
165 ->169 0.11428
166 ->169 0.13631
167 ->170 0.64264

Excited State 7: Singlet-A 3.1563 eV 392.82 nm f=0.8472
<S**2>=0.000
162 ->169 0.16705
165 ->169 -0.10282
166 ->170 0.63392
167 ->169 0.15649

Excited State 8: Singlet-A 3.2985 eV 375.88 nm f=0.0572
<S**2>=0.000
162 ->169 0.23249
163 ->169 0.62499
166 ->170 -0.11184
167 ->170 -0.11385

Excited State 9: Singlet-A 3.3018 eV 375.50 nm f=0.0010
<S**2>=0.000
164 ->169 0.70422

Excited State 10: Singlet-A 3.3672 eV 368.21 nm f=0.0412
<S**2>=0.000
158 ->169 0.19087
160 ->169 0.32782
162 ->169 0.49404
163 ->169 -0.16809
165 ->170 0.20229
168 ->172 -0.10235

TD-DFT of PTZ 4 in DCM solvent. Calculation method: B3LYP/6-31G(d,p)

Excitation energies and oscillator strengths:

Excited State 1: Singlet-A 3.1114 eV 398.48 nm f=2.3897
<S**2>=0.000
124 ->125 0.70011
This state for optimization and/or second-order correction.
Total Energy, E(TD-HF/TD-KS) = -1798.31950823
Copying the excited state density for this state as the 1-particle RhoCI density.

Excited State 2: Singlet-A 3.7183 eV 333.44 nm f=0.0456
<S**2>=0.000
123 ->126 0.14996
124 ->126 0.67563

Excited State 3: Singlet-A 3.7907 eV 327.08 nm f=0.1243
<S**2>=0.000
123 ->125 0.69189

Excited State 4: Singlet-A 4.0814 eV 303.78 nm f=0.0352
<S**2>=0.000
124 ->127 0.67080
124 ->128 0.10187

Excited State 5: Singlet-A 4.3502 eV 285.01 nm f=0.0222
<S**2>=0.000
122 ->126 0.12085
123 ->126 0.57154
124 ->126 -0.12043
124 ->127 -0.11186
124 ->128 0.32686

Excited State 6: Singlet-A 4.3909 eV 282.37 nm f=0.0044
<S**2>=0.000
123 ->126 -0.32937
123 ->128 0.15729
124 ->126 0.12270
124 ->128 0.55296

Excited State 7: Singlet-A 4.3978 eV 281.92 nm f=0.0000
<S**2>=0.000
120 ->125 -0.45195
123 ->130 -0.12385
124 ->130 0.51407

Excited State 8: Singlet-A 4.4880 eV 276.26 nm f=0.0360
<S**2>=0.000
122 ->125 0.66430
124 ->129 -0.16278

Excited State 9: Singlet-A 4.5336 eV 273.48 nm f=0.0001
<S**2>=0.000
118 ->125 0.67046
118 ->127 0.16324

Excited State 10: Singlet-A 4.5558 eV 272.15 nm f=0.0023
<S**2>=0.000
121 ->125 0.57467
121 ->127 0.14222
123 ->131 -0.18634
124 ->131 0.31599

TD-DFT of PTZ 5 in DCM solvent. Calculation method: CAM-B3LYP/6-31G(d,p)

Excitation energies and oscillator strengths:

Excited State 1: Singlet-A 3.0709 eV 403.74 nm f=0.9274
<S**2>=0.000
153 ->157 -0.18660
155 ->157 0.21405
155 ->158 0.15291
156 ->157 0.60913
This state for optimization and/or second-order correction.
Total Energy, E(TD-HF/TD-KS) = -2244.91533187
Copying the excited state density for this state as the 1-particle RhoCI density.

Excited State 2: Singlet-A 3.1813 eV 389.73 nm f=0.5401
<S**2>=0.000
151 ->157 0.13725
152 ->157 -0.12080
155 ->157 0.59898
155 ->158 0.10217
156 ->157 -0.20616
156 ->158 0.17665

Excited State 3: Singlet-A 3.7367 eV 331.80 nm f=0.2581
<S**2>=0.000

153 ->158 -0.19859
155 ->157 -0.18536
155 ->158 0.33978
155 ->160 -0.10452
156 ->158 0.52123

Excited State 4: Singlet-A 3.7762 eV 328.33 nm f=0.5413
<S**2>=0.000
151 ->158 0.10707
152 ->158 -0.10876
153 ->157 0.18100
155 ->158 0.51730
156 ->157 -0.13009
156 ->158 -0.32960
156 ->160 -0.13745

Excited State 5: Singlet-A 4.1645 eV 297.72 nm f=0.0156
<S**2>=0.000
150 ->157 0.50795
150 ->158 -0.19233
151 ->157 0.36679
151 ->158 -0.12430
156 ->162 0.10069

Excited State 6: Singlet-A 4.3216 eV 286.90 nm f=0.0363
<S**2>=0.000
148 ->157 -0.29297
148 ->158 -0.19935
152 ->157 0.22744
152 ->158 0.15322
153 ->157 0.20562
155 ->159 0.40416
156 ->159 0.16360

Excited State 7: Singlet-A 4.4144 eV 280.86 nm f=0.1381
<S**2>=0.000
147 ->157 -0.22136
152 ->157 -0.13997
153 ->157 0.53940
155 ->158 -0.11664

155 ->159 -0.16646
156 ->157 0.18754

Excited State 8: Singlet-A 4.5606 eV 271.86 nm f=0.0172
<S**2>=0.000
149 ->157 0.42133
149 ->158 -0.32931
149 ->160 -0.28321
150 ->157 0.12112
151 ->157 -0.11340
152 ->157 0.18722
155 ->159 -0.13193

Excited State 9: Singlet-A 4.5848 eV 270.42 nm f=0.0884
<S**2>=0.000
145 ->157 -0.14548
148 ->157 -0.10223
149 ->157 -0.22703
149 ->158 0.16848
149 ->160 0.14625
150 ->157 0.18969
151 ->157 -0.17840
152 ->157 0.33233
153 ->158 0.14977
155 ->157 0.11557
155 ->159 -0.28799
156 ->159 -0.12555

Excited State 10: Singlet-A 4.7739 eV 259.71 nm f=0.0296
<S**2>=0.000
145 ->157 -0.10239
148 ->157 0.43580
148 ->158 0.11777
150 ->157 0.11142
151 ->157 -0.21472
153 ->158 0.14362
155 ->159 0.28684
156 ->160 0.18993

TD-DFT of PTZ 6 in gas phase. Calculation method: B3LYP/6-31G(d,p)

Excitation energies and oscillator strengths:

Excited State 1: Singlet-A 2.0382 eV 608.31 nm f=0.1142
<S**2>=0.000
175 ->177 0.64862
176 ->177 -0.25827
This state for optimization and/or second-order correction.
Total Energy, E(TD-HF/TD-KS) = -2476.97227296
Copying the excited state density for this state as the 1-particle RhoCI density.

Excited State 2: Singlet-A 2.0946 eV 591.91 nm f=0.4312
<S**2>=0.000
174 ->177 0.21628
175 ->177 0.26238
176 ->177 0.60116
176 ->178 0.15554

Excited State 3: Singlet-A 2.5609 eV 484.14 nm f=0.1125
<S**2>=0.000
174 ->177 -0.48186
175 ->178 0.14473
176 ->178 0.48205

Excited State 4: Singlet-A 2.8123 eV 440.86 nm f=0.6184
<S**2>=0.000
172 ->177 0.13580
174 ->177 0.38511
175 ->178 -0.20806
176 ->177 -0.22208
176 ->178 0.47448

Excited State 5: Singlet-A 3.0633 eV 404.74 nm f=0.9158
<S**2>=0.000
172 ->177 -0.13967
174 ->177 0.19778
174 ->178 0.15720
175 ->178 0.61985
176 ->177 -0.14098

Excited State 6: Singlet-A 3.1944 eV 388.13 nm f=0.0002
<S**2>=0.000
173 ->177 0.70618

Excited State 7: Singlet-A 3.2055 eV 386.79 nm f=0.1031
<S**2>=0.000
172 ->177 0.62730
174 ->178 -0.19402
175 ->178 0.19581

Excited State 8: Singlet-A 3.2993 eV 375.79 nm f=0.0048
<S**2>=0.000
168 ->177 0.18303
170 ->177 0.51022
171 ->177 -0.35645
174 ->178 0.24100

Excited State 9: Singlet-A 3.3125 eV 374.29 nm f=0.0051
<S**2>=0.000
168 ->177 -0.27308
170 ->177 0.47623
171 ->177 0.37303
174 ->178 -0.22327

Excited State 10: Singlet-A 3.4175 eV 362.79 nm f=0.0721
<S**2>=0.000
167 ->177 0.14129
171 ->177 0.29895
172 ->177 0.19077
174 ->177 -0.12591
174 ->178 0.53730
176 ->181 0.10326