Electronic Supplementary Information (ESI)

Electropolymerized Organic N/P Bipolar Cathode Toward High Energy and High Power Density Sodium Dual-Ion Batteries

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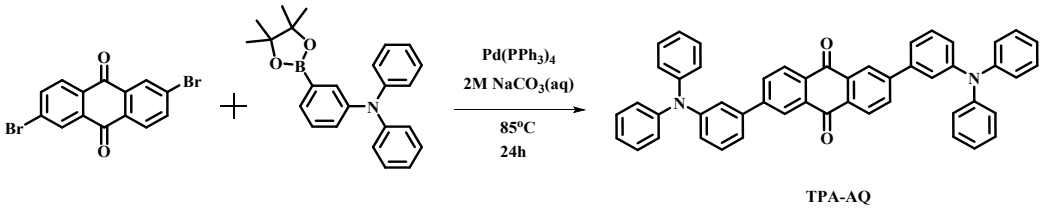
Contents

1. Experimental Procedures

Materials and Characterization: All starting chemicals and solvents were obtained from Energy Chemical or Aladdin, and used without further purification. Nuclear magnetic resonances (^{1}H NMR) were conducted on Bruker Avance III 400MHz. Transform Infrared Spectroscopy (FTIR) was recorded with Bruker 46 TENSOR Π. Thermal gravimetric analysis (TGA) was carried out with Hitachi 7300 at a heating rate of 10 ℃ min^{-1}under nitrogen atmosphere. The microstructure and morphology were observed by high-resolution cold field-emission scanning electron microscopy (SEM, Regulus 8230) equipped with energy dispersive spectroscopy (EDS) for elemental analysis. X-ray diffraction (XRD) patterns were collected on a Rigaku Ultima IV using Cu Kα radiation (λ= 1.5406 Å, 40 kV and 40 mA). Ultraviolet-visible spectroscopy (UV-vis, FS5 spectrofluorometer, Edinburgh Instruments Ltd.)) and X-ray photoelectron spectroscopy (XPS, Thermo Scientific K-Alpha, USA) was applied to analyze the chemical composition of the pristine and cycled electrode. The cycled electrodes used for the characterization were washed with Propylene carbonate (PC) and dried.

Synthesis of TPA-AQ: 2,6-bis(3-(diphenylamino)phenyl)anthracene-9,10-dione (TPA-AQ) was synthesized by Suzuki coupling between AQ-Br_2 and N,N-Diphenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)aniline with a yield of 73%.[1-4]



Scheme 1 Synthetic routes of TPA-AQ.

2. Supplementary Data

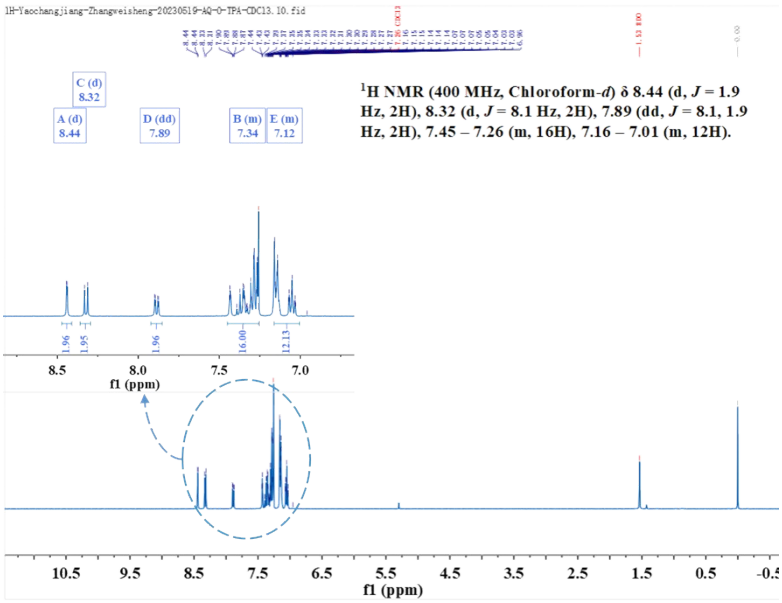


Fig. S1 ^{1}H NMR spectra ($CDCl_3$, 400 MHz) 8.44 (d, J=1.9 Hz, 2H) 8.32(d, J=8.1 Hz, 2H),7.89 (dd, J= 8.1,1.9 Hz, 2H),7.44-7.24 (m,16H),7.17-7.13 (m, 8H),7.09-6.99 (m, 4H).

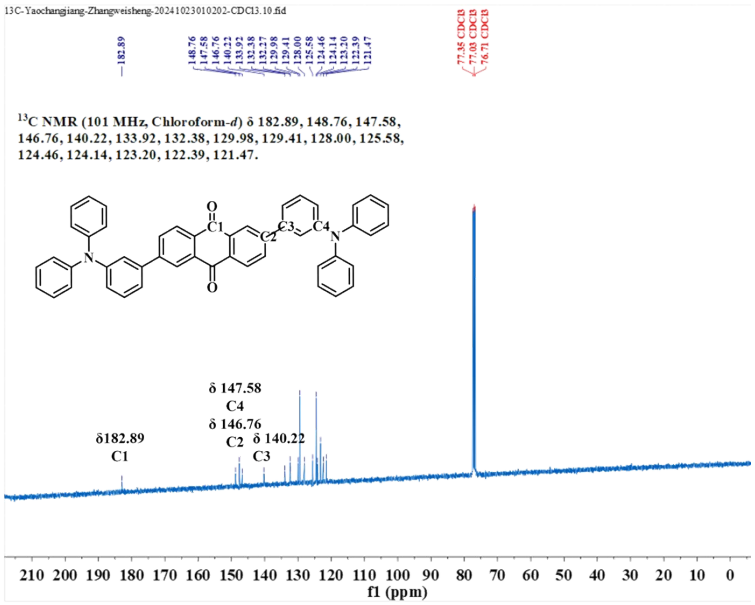


Fig. S2 ^{13}C NMR spectra ($CDCl_3$, 101 MHz) δ 182.89, 148.76, 147.58, 146.76, 140.22, 133.92, 132.38, 129.98, 129.41, 128.00, 125.58, 124.46, 124.14, 123.20, 122.39, 121.47.

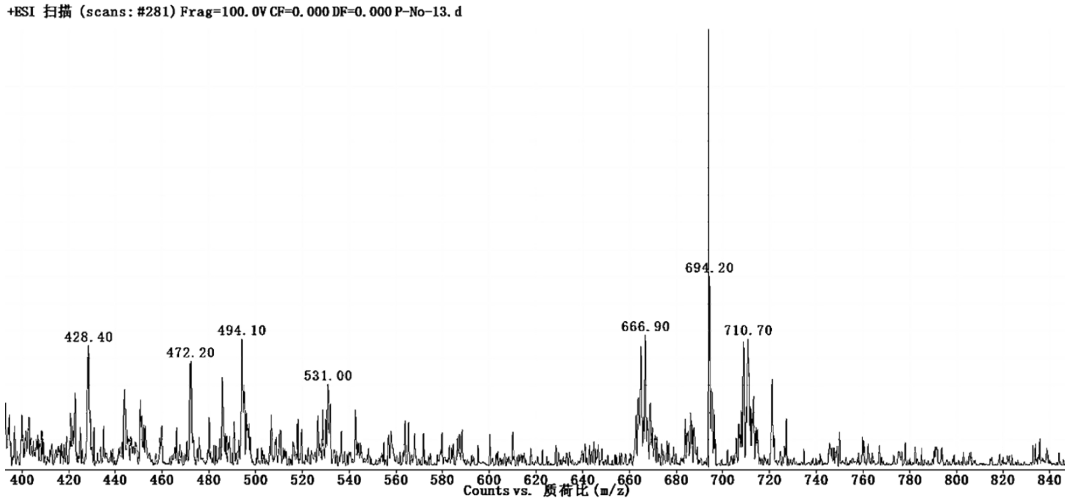


Fig. S3 LC-MS (ESI) m/z: TPA-AQ for $C_{50}H_{34}N_2O_2$, 694.2; found, 694.2.

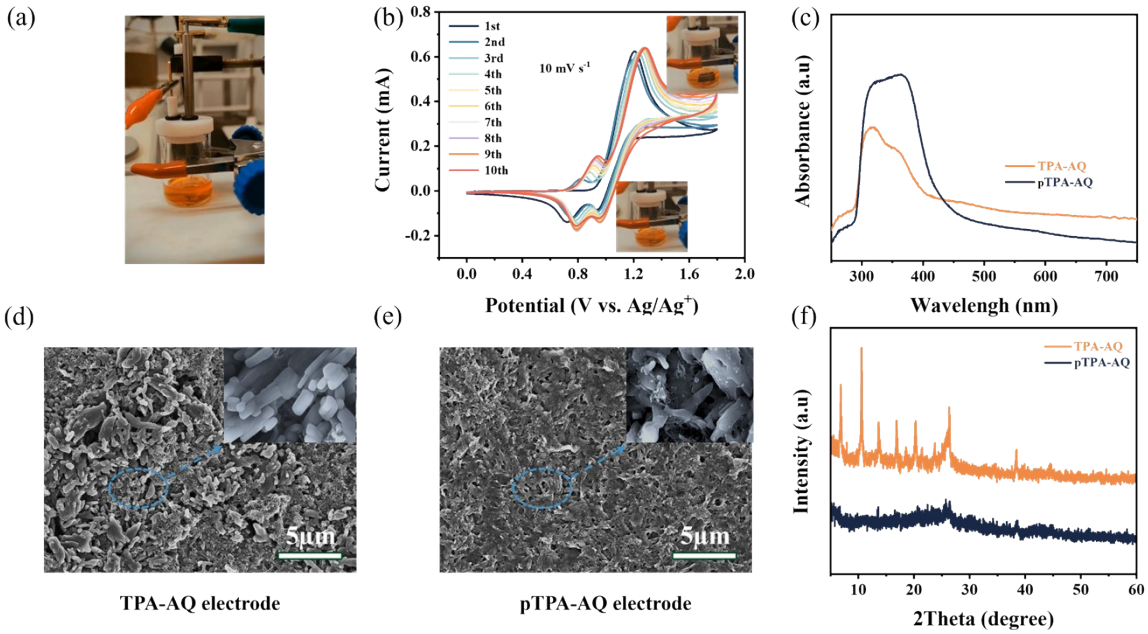


Fig. S4 (a) Three-electrode system, (b) cyclic voltammograms, (c) UV–vis spectra, (d) SEM images of TPA-AQ electrode, (e) SEM images of pTPA-AQ electrode, (f) XRD pattern of TPA-AQ and pTPA-AQ electrode.

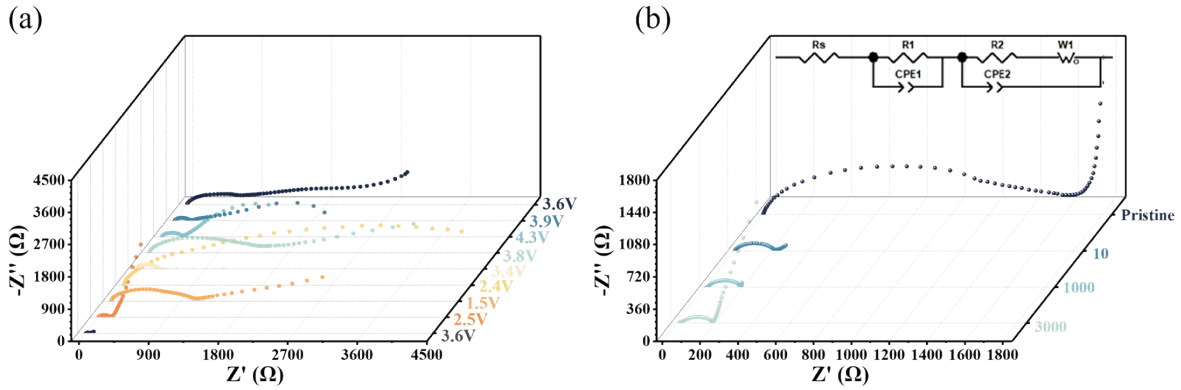


Fig. S5 (a) *In situ* EIS profiles of pTPA-AQ cathode in the first cycle, (2) the EIS profiles after different number of cycles (open circuit voltage ~ 3.4V).

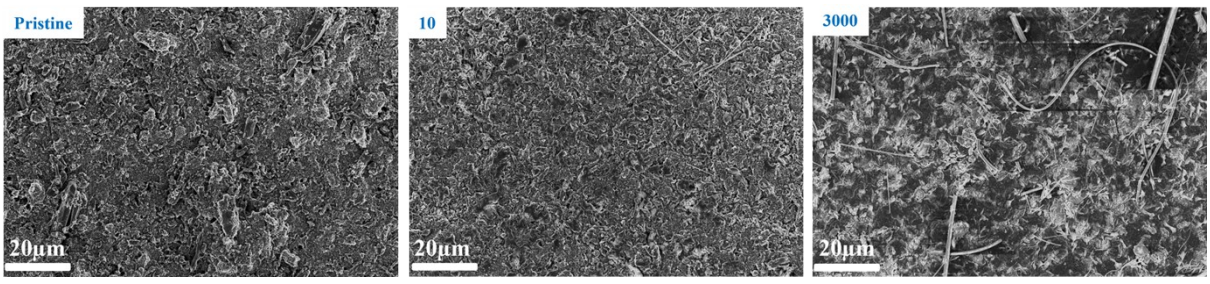


Fig. S6 SEM images of the electrode surface after different cycles.

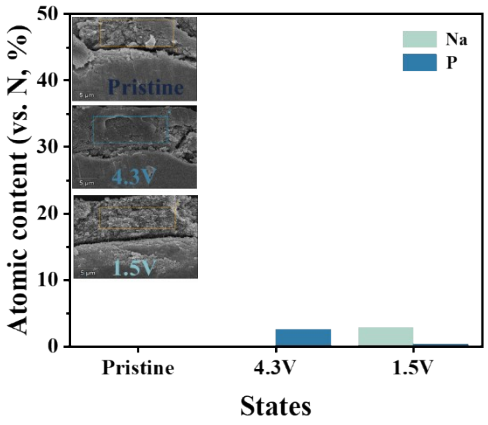


Fig. S7 Energy-dispersive spectroscopy (EDS) on the electrode surface in the pristine, 4.3V and 1.5V states compared to the N element.

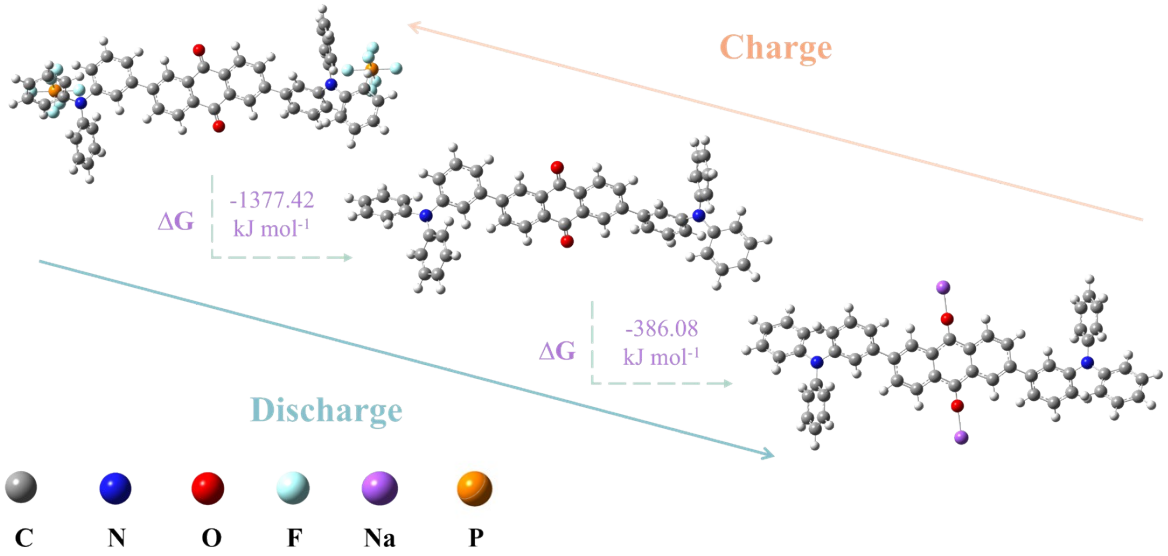


Fig. S8 Electronic structure and Gibbs free energy calculations of TPA-AQ in the pristine, full charge and full discharge states.

3. The calculation results of TPA-AQ.

All calculations presented in this paper are performed using the Gaussian 16 software[5] at the B3LYP/6-31+G (d,p) level level of theory.

TPA-AQ

Symbolic Z-matrix:

Charge = 0 Multiplicity = 1

Symbol	X	Y	Z
C	-1.0835	-0.8053	-2.9571
C	-0.9359	0.6507	-3.1218
C	0.2417	1.2871	-2.6851
C	1.3194	0.4978	-2.062
C	1.166	-0.9577	-1.8841
C	-0.0114	-1.5924	-2.3256
C	-0.1506	-2.9813	-2.1581
C	0.8756	-3.733	-1.5658
C	2.0617	-3.1146	-1.1246
C	2.188	-1.72	-1.2855
C	-1.9686	1.4097	-3.7045
C	-1.8584	2.8065	-3.8587
C	-0.6706	3.4277	-3.4235
C	0.3671	2.6785	-2.8454
C	3.1559	-3.9217	-0.5314
C	-2.9752	3.6051	-4.4298
C	3.3488	-5.2578	-0.9357
C	4.3965	-6.0361	-0.4116
C	4.0374	-3.3777	0.4245
C	5.0815	-4.1504	0.9602
C	5.2665	-5.4771	0.5404
N	4.5937	-7.3633	-0.8818
C	3.505	-8.2821	-0.8396
C	5.7898	-7.6843	-1.587
C	2.7873	-8.4729	0.357
C	1.697	-9.358	0.4005
C	1.3129	-10.058	-0.7547
C	2.0215	-9.871	-1.9526
C	3.112	-8.9863	-1.9945
C	6.4133	-8.9328	-1.3979
C	7.5881	-9.2555	-2.0976
C	8.1514	-8.331	-2.9921
C	7.5371	-7.0835	-3.1857

C	6.3619	-6.7629	-2.4866
C	-2.7345	4.8453	-5.0567
C	-3.7856	5.6501	-5.5415
C	-5.1078	5.1835	-5.418
C	-5.3657	3.94	-4.8219
C	-4.3087	3.1602	-4.3272
N	-3.5106	6.9305	-6.1158
C	-2.4137	7.7082	-5.6474
C	-4.384	7.5067	-7.0812
C	-4.9663	8.767	-6.8448
C	-4.6678	6.8304	-8.2828
C	-5.5266	7.4059	-9.2344
C	-5.8255	9.3426	-7.7954
C	-6.1065	8.662	-8.9914
C	-2.2611	7.9744	-4.273
C	-1.1749	8.7381	-3.8148
C	-0.2362	9.2444	-4.7288
C	-0.3863	8.9873	-6.1014
C	-1.4724	8.2228	-6.559
O	-2.2199	-1.4255	-3.3807
O	2.4567	1.1177	-1.6407
H	-1.0247	-3.4715	-2.4757
H	0.7326	-4.7669	-1.4429
H	3.0729	-1.2404	-0.9828
H	-2.8341	0.9164	-4.0385
H	-0.5536	4.4695	-3.4949
H	1.2352	3.1748	-2.5209
H	2.7318	-5.6783	-1.6756
H	3.9151	-2.3904	0.763
H	5.7289	-3.7324	1.6749
H	6.0554	-6.047	0.9375
H	3.0659	-7.954	1.228
H	1.1677	-9.4951	1.298
H	0.4963	-10.718	-0.7232

H	1.7333	-10.390	-2.8197
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H	6.0042	-9.6312	-0.7268
H	8.0468	-10.189	-1.9502
H	9.0303	-8.5724	-3.5153
H	7.955	-6.3905	-3.8563
H	5.9078	-5.8291	-2.6507
H	-1.7462	5.1824	-5.1734
H	-5.9145	5.7661	-5.7561
H	-6.3561	3.6014	-4.7252
H	-4.5379	2.2536	-3.8485
H	-4.7663	9.2823	-5.9505
H	-4.234	5.8923	-8.4752
H	-5.7344	6.8963	-10.129
H	-6.2586	10.2823	-7.6114
H	-6.7488	9.0919	-9.7034
H	-2.9618	7.6045	-3.5819
H	-1.0654	8.9321	-2.7877
H	0.5765	9.8159	-4.3862
H	0.3151	9.3659	-6.7864
H	-1.5735	8.0303	-7.5876

TPA-AQ-Na_2

Symbolic Z-matrix:

Charge = 0 Multiplicity = 1

Symbol	X	Y	Z
C	0.15139	1.09056	0.20778
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C	-0.83328	-0.9616	-0.9197
C	0.4394	-1.4599	-1.2309
C	1.57314	-0.7363	-0.8403
C	1.42448	0.58406	-0.0888
C	2.58268	1.26311	0.28972

C	3.80511	0.74586	-0.0176
C	3.94197	-0.4736	-0.7220
C	2.85891	-1.1957	-1.1233
C	-2.26857	0.82401	0.10456
C	-3.35057	0.08601	-0.27096
C	-3.21177	-1.14412	-0.95532
C	-1.99001	-1.6544	-1.27414
C	5.35288	-0.99904	-1.0444
C	-4.76413	0.60033	0.05833
C	6.48178	-0.28459	-0.62171
C	7.76563	-0.76137	-0.9207
C	5.50771	-2.19309	-1.76084
C	6.79106	-2.66883	-2.06178
C	7.92036	-1.95263	-1.64207
N	8.94952	-0.0106	-0.47755
C	8.61887	1.41952	-0.40834
C	9.36553	-0.48198	0.85153
C	8.80964	2.23751	-1.53003
C	8.49046	3.60025	-1.46533
C	7.98279	4.14544	-0.27868
C	7.79323	3.32803	0.84365
C	8.11181	1.96489	0.77896
C	10.71716	-0.43051	1.21973
C	11.11656	-0.87909	2.4858
C	10.16465	-1.37929	3.38438
C	8.81303	-1.43052	3.01656
C	8.41352	-0.98195	1.75011
C	-5.88528	-0.16221	-0.29568
C	-7.17204	0.2975	0.01317
C	-7.33963	1.52781	0.66259
C	-6.21841	2.29257	1.01281
C	-4.93068	1.82782	0.71254
N	-8.34375	-0.51539	-0.34198
C	-8.65527	-1.42215	0.77226

C	-9.49758	0.35965	-0.60021
C	-9.74532	0.83075	-1.89712
C	-10.35121	0.72148	0.45073
C	-11.45393	1.55074	0.20491
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C	-11.7026	2.01957	-1.09224
C	-8.36628	-1.03739	2.08863
C	-8.66096	-1.90117	3.15212
C	-9.24359	-3.15011	2.89901
C	-9.53345	-3.53426	1.58283
C	-9.23968	-2.67017	0.51934
O	0.02263	2.22375	0.83517
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H	2.99484	-2.11499	-1.65405
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H	-1.91802	-2.58615	-1.7951
H	6.36347	0.62477	-0.07066
H	4.64554	-2.74162	-2.07864
H	6.90871	-3.57935	-2.61214
H	8.90025	-2.31557	-1.87255
H	9.19873	1.82194	-2.4357
H	8.63443	4.22455	-2.32212
H	7.73966	5.1859	-0.22934
H	7.40514	3.74456	1.74971
H	7.96749	1.34047	1.63596
H	11.44386	-0.04855	0.53403
H	12.14818	-0.83937	2.76658
H	10.46934	-1.72173	4.35129
H	8.08615	-1.81198	3.70286
H	7.38171	-1.02126	1.46968
H	-5.75862	-1.09731	-0.80054

H	-8.32292	1.88278	0.89146
H	-6.3458	3.2315	1.51003
H	-4.07537	2.41036	0.98255
H	-9.09322	0.55669	-2.69967
H	-10.16092	0.36429	1.44107
H	-12.10601	1.8258	1.00736
H	-11.03746	2.01925	-3.13325
H	-12.54487	2.65192	-1.28005
H	-7.92032	-0.08378	2.28213
H	-8.44091	-1.60709	4.15718
H	-9.46709	-3.81033	3.71054
H	-9.97908	-4.48737	1.38966
H	-9.46139	-2.96346	-0.48535
Na	-1.35062	3.61311	0.1792
Na	1.94448	-3.9817	-1.24931

TPA-AQ-$(PF_6)_2$

Symbolic Z-matrix:

Charge = 0 Multiplicity = 1

Symbol	X	Y	Z
C	0.31848	-1.6115	0.08386
C	1.44392	-0.6898	0.41098
C	1.20403	0.61227	0.88402
C	-0.17698	1.12544	1.07813
C	-1.30115	0.20801	0.73965
C	-1.06121	-1.09461	0.2664
C	-2.15251	-1.91623	-0.03793
C	-3.4497	-1.45191	0.12738
C	-3.71189	-0.14843	0.60477
C	-2.60795	0.66556	0.90368
C	2.75111	-1.14581	0.24127
C	3.85398	-0.32981	0.53312
C	3.59187	0.97583	1.00409

C	2.2944	1.43798	1.1776
C	-5.10344	0.34585	0.78105
C	5.24611	-0.82888	0.34598
C	-7.5012	-0.05052	0.82533
C	-5.36353	1.70335	1.10269
C	-6.66807	2.18402	1.22186
C	-7.74577	1.32687	1.07353
N	-8.61847	-0.87661	0.73767
C	-8.59996	-2.05983	-0.08949
C	-9.72005	-0.57435	1.55528
C	-9.26559	-2.10074	-1.31645
C	-9.13548	-3.25365	-2.10116
C	-8.37493	-4.34186	-1.66928
C	-7.76741	-4.30859	-0.4104
C	-7.888	-3.1708	0.38563
C	-11.04876	-0.6221	1.09165
C	-12.0838	-0.37616	1.98529
C	-11.82827	-0.09335	3.33431
C	-10.50534	-0.02272	3.79378
C	-9.45772	-0.25635	2.91716
C	6.34738	-0.07121	0.75188
C	7.65186	-0.5555	0.58205
C	7.89434	-1.81114	-0.00821
C	6.80377	-2.5666	-0.41166
C	5.50178	-2.09142	-0.23873
N	8.73169	0.23707	0.97491
C	8.69491	1.62408	0.83067
C	9.83519	-0.3506	1.6054
C	11.12567	-0.03515	1.16043
C	9.62706	-1.239	2.68241
C	10.72118	-1.78205	3.34135
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C	12.01944	-1.44974	2.92598
C	8.01788	2.21664	-0.25372

C	8.0193	3.59631	-0.38193
C	8.6858	4.40351	0.55104
C	9.3618	3.81498	1.62831
C	9.3697	2.43509	1.77405
O	0.52617	-2.75135	-0.31752
O	-0.38411	2.25745	1.50125
H	-1.96321	-2.91754	-0.41004
H	-4.26483	-2.11432	-0.1375
H	-2.72318	1.67399	1.27871
H	2.86702	-2.15922	-0.12027
H	4.40552	1.65292	1.23211
H	2.10426	2.44351	1.5377
H	-7.4661	-3.14102	1.38769
H	-4.54641	2.40658	1.20035
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H	-8.75972	1.67923	0.92266
H	-9.94292	-1.3129	-1.63691
H	-9.64747	-3.28881	-3.05797
H	-8.28105	-5.22326	-2.29623
H	-7.21392	-5.16667	-0.04071
H	-11.27699	-0.65572	0.03278
H	-13.10153	-0.35378	1.60948
H	-12.65306	0.09076	4.01587
H	-10.2959	0.19443	4.83645
H	-8.43205	-0.25262	3.26967
H	6.22118	0.88982	1.23263
H	8.9103	-2.12619	-0.21667
H	6.96787	-3.51965	-0.90334
H	4.68222	-2.70803	-0.58572
H	8.61705	-1.46324	3.00867
H	10.5661	-2.45097	4.18225
H	13.20959	-0.39059	1.46379
H	12.87775	-1.87435	3.43865
H	7.58567	1.59338	-1.02451

H	7.53592	4.04654	-1.24282
H	8.6882	5.48263	0.43224
H	9.86981	4.43677	2.35879
H	9.86944	1.97423	2.61757
P	-10.67811	1.80647	-1.92242
P	10.27259	-0.22407	-2.51896
F	10.04511	-1.53025	-3.45906
F	9.98787	0.79243	-3.75839
F	11.87444	-0.23212	-2.81544
F	10.49317	1.10075	-1.51055
F	8.65675	-0.22115	-2.13312
F	10.52181	-1.20588	-1.1982
F	-10.11734	3.33021	-2.04319
F	-12.05323	2.19606	-2.69421
F	-11.37216	2.14352	-0.46479
F	-11.21627	0.2262	-1.75972
F	-9.95254	1.38009	-3.32119
F	-9.29888	1.36344	-1.09927
H	11.23727	0.48552	0.20857
C	-6.19189	-0.51791	0.63859
H	-6.04254	-1.55714	0.39613

4. References

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