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Supporting Information

Phosphorus-Based Heteropentacenes: Efficiently Tunable Materials for Organic *n*-Type Semiconductors

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Contents:

1) Solid State organization

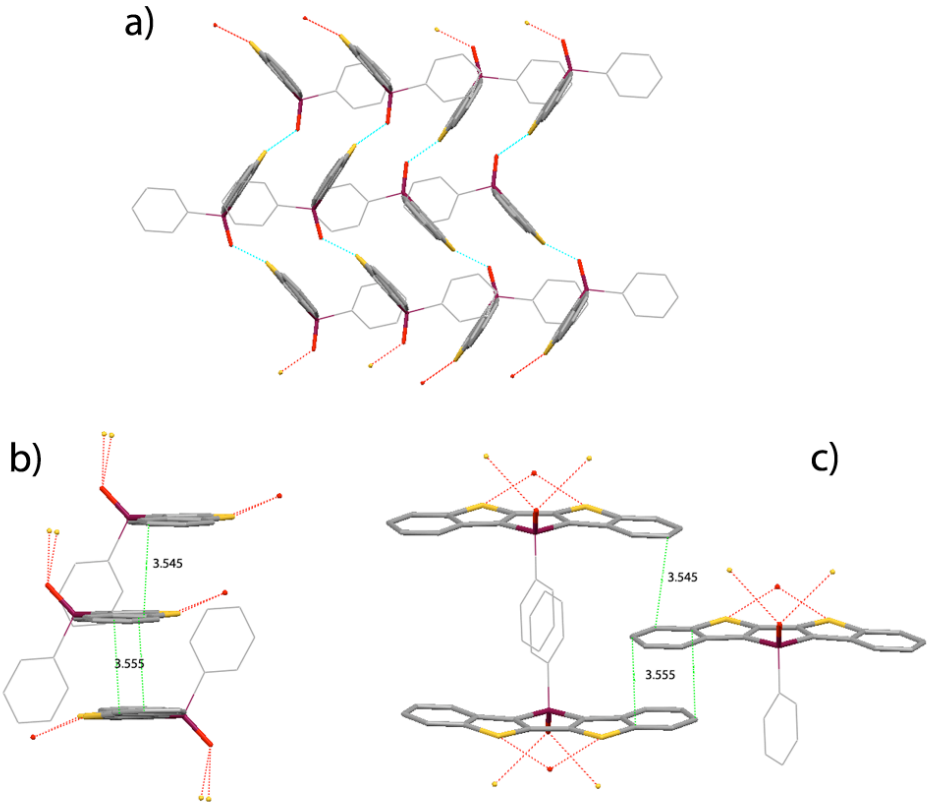


Figure S1. Molecular packing of **4** in the solid state (top: overall herringbone pattern; bottom: two views of π-stacking within layers).

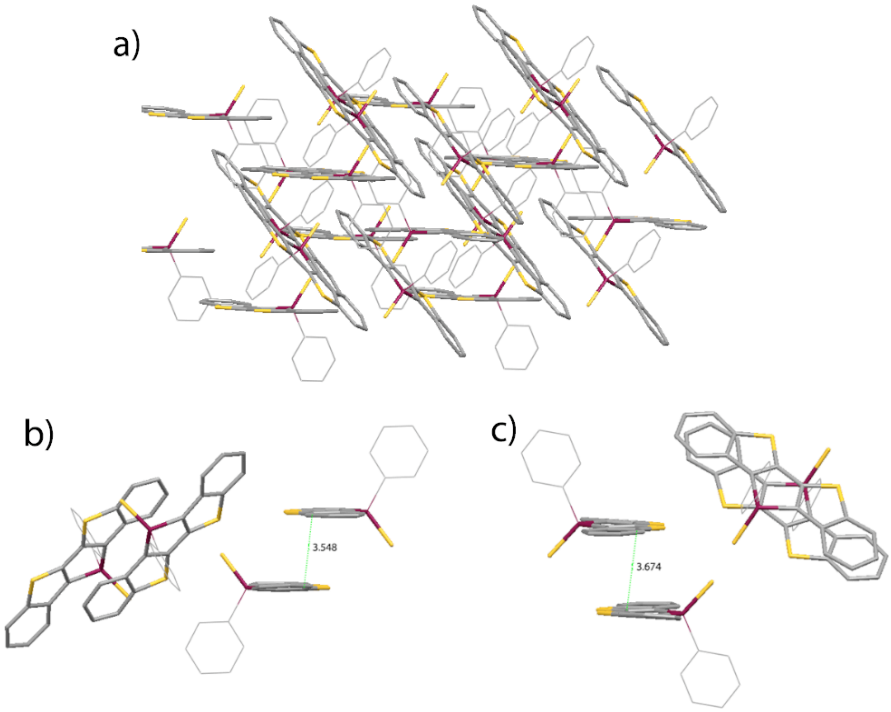


Figure S2. Molecular packing of **5** in the solid state (top: overall structure; bottom: views of the π-stacking between the two independent molecules of the unit cell).

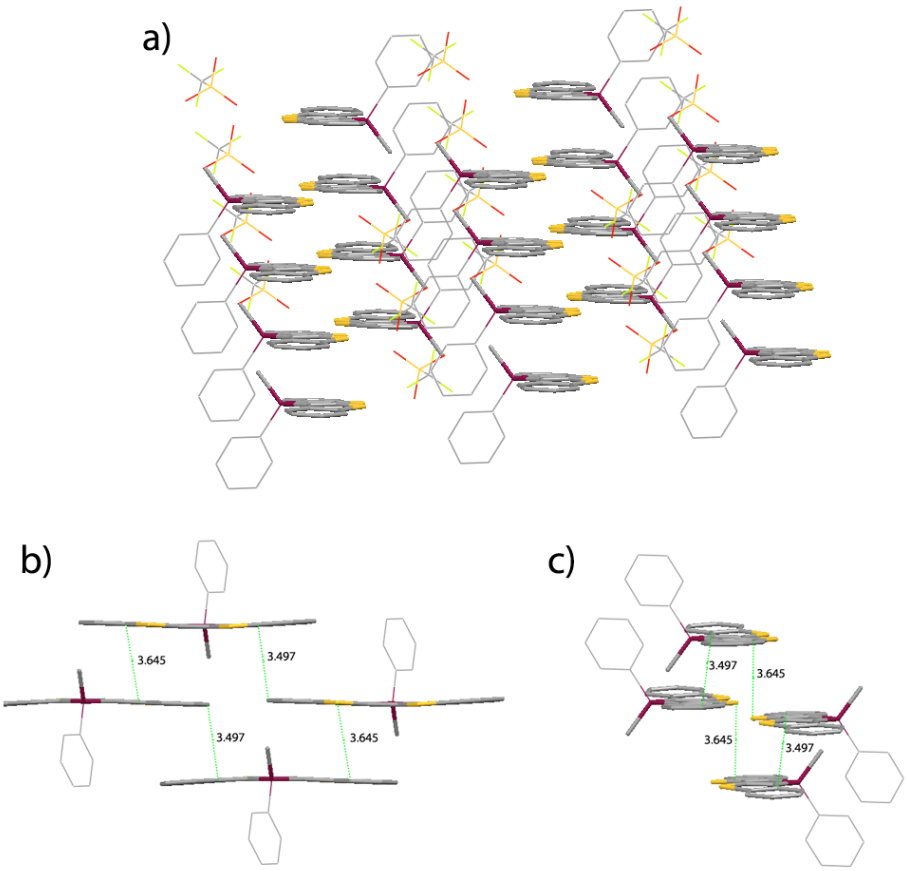
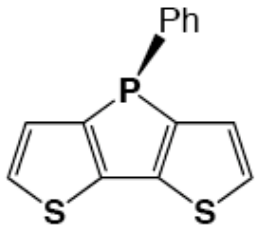


Figure S3. Molecular packing of **8** in the solid state (top) and two views of the π-stacking interactions (bottom; anions are omitted for clarity).

2) HOMO – LUMO energies of neutral, cationic, and anionic species



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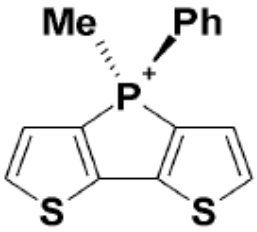
Charge e	Multiplicity	E_{tot} hartree	E_{rel} kcal/mol	ε(HOMO) eV	ε(LUMO) eV	ΔE(HOMO,LUMO) eV	Symmetry	Remarks
-1	doublet	-1676.64695	0.0	0.88	2.27	1.39	C_1	HOMO → SOMO
0	singlet	-1676.63412	8.1	-5.67	-1.62	4.06	C_s	
+1	doublet	-1676.37570	170.2	-10.13	-6.33	3.80	C_s	HOMO → SOMO



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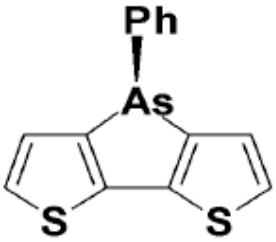
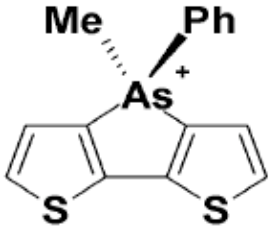
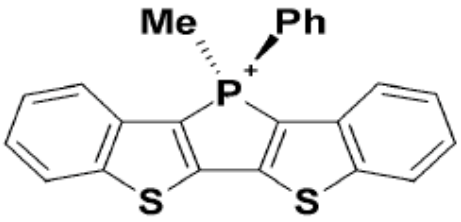
Charge e	Multiplicity	E_{tot} hartree	E_{rel} kcal/mol	ε(HOMO) eV	ε(LUMO) eV	ΔE(HOMO,LUMO) eV	Symmetry	Remarks
0	doublet	-1716.49481	0.0	-3.17	-1.38	1.79	C_1	HOMO → SOMO
+1	singlet	-1716.33268	101.7	-9.44	-5.66	3.78	C_s	



Charge e	Multiplicity	E_{tot} hartree	E_{rel} kcal/mol	ε(HOMO) eV	ε(LUMO) eV	ΔE(HOMO,LUMO) eV	Symmetry	Remarks
-1	doublet	-3569.10010	0.0	0.88	2.24	1.36	C_1	HOMO → SOMO
0	singlet	-3569.08697	8.2	-5.69	-1.63	4.06	C_s	
+1	doublet	-3568.82847	170.5	-10.08	-6.33	3.75	C_s	HOMO → SOMO

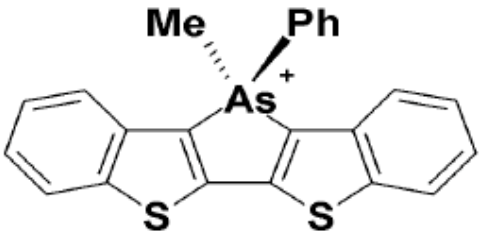


Charge e	Multiplicity	E_{tot} hartree	E_{rel} kcal/mol	ε(HOMO) eV	ε(LUMO) eV	ΔE(HOMO,LUMO) eV	Symmetry	Remarks
0	doublet	-3608.92924	0.0	-3.02	-1.45	1.57	C_1	B3LYP/6-31+G*
+1	singlet	-3608.77248	98.4	-9.39	-5.53	3.86	C_s	B3LYP/6-31+G*
0	doublet	-3611.14354	0.0	-3.12	-1.40	1.72	C_1	B3LYP/6-311+G*
+1	singlet	-3610.98502	99.5	-9.43	-5.55	3.88	C_s	B3LYP/6-311+G*

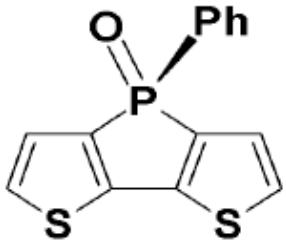


cation of 8

Charge *e*	Multiplicity	E_{tot} *hartree*	E_{rel} *kcal/mol*	ε(HOMO) *eV*	ε(LUMO) *eV*	ΔE(HOMO,LUMO) *eV*	Symmetry	Remarks
0	doublet	-2023.81413	0.0	-3.51	-1.52	1.99	C_s	HOMO → SOMO
+1	singlet	-2023.64552	105.8	-8.94	-5.66	3.28	C_s	



Charge *e*	Multiplicity	E_{tot} *hartree*	E_{rel} *kcal/mol*	ε(HOMO) *eV*	ε(LUMO) *eV*	ΔE(HOMO,LUMO) *eV*	Symmetry	Remarks
0	doublet	-3916.18606	0.0	-3.16	-1.09	2.07	C_s	HOMO → SOMO
+1	singlet	-3916.02923	98.4	-8.72	-5.37	3.35	C_s	



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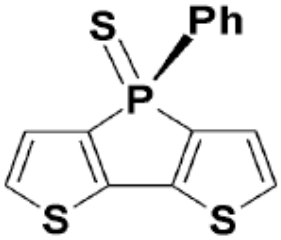
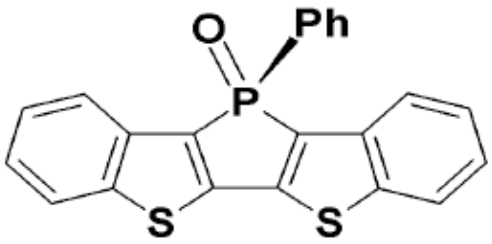
Charge *e*	Multiplicity	E_{tot} *hartree*	E_{rel} *kcal/mol*	ε(HOMO) *eV*	ε(LUMO) *eV*	ΔE(HOMO,LUMO) *eV*	Symmetry	Remarks
-1	doublet	-1751.91279	0.0	0.37	2.05	1.68	C_1	HOMO → SOMO
0	singlet	-1751.88053	20.2	-6.03	-2.15	3.88	C_s	
+1	doublet	-1751.60952	190.3	-10.35	-6.85	3.50	C_s	HOMO → SOMO



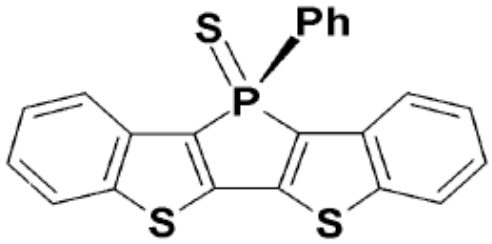
B/3

Charge *e*	Multiplicity	E_{tot} *hartree*	E_{rel} *kcal/mol*	ε(HOMO) *eV*	ε(LUMO) *eV*	ΔE(HOMO,LUMO) *eV*	Symmetry	Remarks
-1	doublet	-2074.87993	0.0	0.24	1.92	1.68	C_1	HOMO → SOMO
0	singlet	-2074.84512	21.8	-5.98	-2.16	3.82	C_s	
+1	doublet	-2074.57700	190.1	-10.14	-6.58	3.56	C_s	HOMO → SOMO



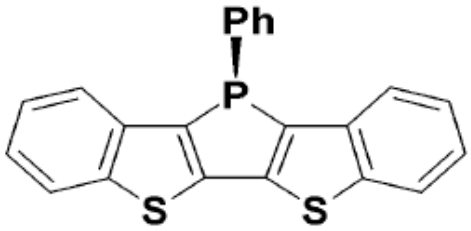
4

Charge *e*	Multiplicity	E_{tot} *hartree*	E_{rel} *kcal/mol*	ε(HOMO) *eV*	ε(LUMO) *eV*	ΔE(HOMO,LUMO) *eV*	Symmetry	Remarks
-1	doublet	-2059.24018	0.0	-0.25	1.82	2.07	C_1	HOMO → SOMO
0	singlet	-2059.19193	30.3	-5.85	-2.39	3.46	C_s	
+1	doublet	-2058.93467	191.7	-9.55	-6.38	3.17	C_s	HOMO → SOMO



5

Charge *e*	Multiplicity	E_{tot} *hartree*	E_{rel} *kcal/mol*	ε(HOMO) *eV*	ε(LUMO) *eV*	ΔE(HOMO,LUMO) *eV*	Symmetry	Remarks
-1	doublet	-2382.20622	0.0	-0.32	1.68	2.00	C_1	HOMO → SOMO
0	singlet	-2382.15443	32.5	-5.88	-2.44	3.44	C_s	
+1	doublet	-2381.89233	197.0	-9.61	-6.18	3.43	C_s	HOMO → SOMO



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Charge *e*	Multiplicity	E_{tot} *hartree*	E_{rel} *kcal/mol*	ε(HOMO) *eV*	ε(LUMO) *eV*	ΔE(HOMO,LUMO) *eV*	Symmetry	Remarks
-1	doublet	-1983.97796	0.0	0.21	1.94	1.73	C_1	HOMO → SOMO
0	singlet	-1983.94632	19.9	-5.60	-1.95	3.65	C_s	
+1	doublet	-1983.69833	175.5	-9.35	-5.94	3.41	C_s	HOMO → SOMO

B3LYP/6-31+G* data for isolated molecules *-unless otherwise indicated*

3) Optimized calculated structures

Compound **3 neutral -** Etot(B3LYP/6-31+G*) = -1983.94631970 au

C	-2.182767	-2.968795	3.283579
C	-1.346360	-2.146564	2.523503
C	-1.846653	-1.012172	1.823360
C	-3.222681	-0.721564	1.909940
C	-4.053879	-1.538553	2.667336
C	-3.539587	-2.656917	3.350036
C	-0.799877	-0.334536	1.109649
C	0.435314	-0.928412	1.280003
S	0.397826	-2.342772	2.309507
P	-0.651193	1.236291	0.171156
C	1.116938	0.847186	-0.133281
C	1.509493	-0.266177	0.583467
S	3.223711	-0.600607	0.477104
C	3.436696	0.802202	-0.577999
C	2.211000	1.489382	-0.807764
C	2.226783	2.638045	-1.623685
C	3.423857	3.071491	-2.181491
C	4.624463	2.376242	-1.943821
C	4.639867	1.237377	-1.140457
C	-1.481608	0.878683	-1.449486
C	-2.387324	1.829251	-1.942501
C	-3.046873	1.619415	-3.159143
C	-2.804618	0.456292	-3.891389
C	-1.901741	-0.497881	-3.406179
C	-1.244519	-0.288711	-2.193758
H	-2.578379	2.736894	-1.374196
H	-3.746559	2.364261	-3.530015
H	-3.315354	0.290527	-4.836633
H	-1.710739	-1.405067	-3.974130
H	-0.544888	-1.033169	-1.822602
H	1.303389	3.179497	-1.811790
H	-3.626661	0.140108	1.385029
H	3.433897	3.958570	-2.809204
H	-5.114580	-1.311588	2.733929
H	5.550733	2.730071	-2.388341
H	-4.204669	-3.284160	3.937405
H	5.567732	0.702876	-0.955300
H	-1.786165	-3.830822	3.813226

Compound **3 radical anion** - Etot(B3LYP/6-31+G*) = -1983.97796114 au

C	-1.538534	-0.640556	-1.963449
C	-1.836322	0.500306	-1.201109
C	-2.778429	1.410473	-1.700954
C	-3.399169	1.201200	-2.938168
C	-3.090545	0.064445	-3.689321
C	-2.158821	-0.857398	-3.195764
P	-1.024520	0.877281	0.461466
C	0.719678	1.202337	-0.003125
C	1.548585	0.105995	0.344354
S	3.253871	0.427167	0.003573
C	2.848659	2.052027	-0.603418
C	1.437962	2.308202	-0.526387
C	0.986977	3.577905	-0.971226
C	1.893377	4.518057	-1.457112
C	3.268983	4.239816	-1.527162
C	3.747802	2.990785	-1.093312
C	0.871547	-0.967112	0.933022
C	-0.528003	-0.774879	1.068378
C	-1.180256	-1.843030	1.738071
C	-0.270977	-2.892248	2.103372
S	1.400734	-2.508329	1.620033
C	-2.545539	-2.023607	2.079721
C	-2.960403	-3.178300	2.740529
C	-2.050431	-4.193074	3.082023
C	-0.689924	-4.043245	2.758559
H	-3.030813	2.291536	-1.111821
H	-4.126073	1.921599	-3.310091
H	-3.573379	-0.105875	-4.649733
H	-1.916199	-1.747544	-3.773716
H	-0.818355	-1.359541	-1.580712
H	-0.074402	3.811430	-0.927894
H	-3.265795	-1.250189	1.822369
H	1.525545	5.486764	-1.792247
H	-4.012907	-3.295600	2.994412
H	3.962688	4.982476	-1.914372
H	-2.391107	-5.089858	3.594245
H	4.811604	2.764888	-1.138245
H	0.026017	-4.819295	3.022976

Compound **3 radical cation** - Etot(B3LYP/6-31+G*) = -1983.69833169 au

C	-1.311997	-0.341982	-2.157531
C	-1.836500	0.540933	-1.196766
C	-3.050974	1.199792	-1.449121
C	-3.733220	0.978002	-2.649269
C	-3.206879	0.099923	-3.599233
C	-1.996565	-0.559543	-3.352747
P	-1.013499	0.898698	0.412328
C	0.755519	1.177376	-0.013566
C	1.598362	0.162908	0.511621
S	3.293547	0.474045	0.285958
C	2.899215	1.985799	-0.554102
C	1.488449	2.221950	-0.624232
C	1.019150	3.402824	-1.254208
C	1.932582	4.297918	-1.785229
C	3.316796	4.041866	-1.703290
C	3.813192	2.886515	-1.086295
C	0.896691	-0.901667	1.107260
C	-0.514012	-0.748775	1.064104
C	-1.191248	-1.843583	1.650609
C	-0.274191	-2.828704	2.139972
S	1.419050	-2.369831	1.877347
C	-2.583905	-2.063591	1.804468
C	-3.023994	-3.221950	2.422574
C	-2.100288	-4.176609	2.895572
C	-0.718742	-3.989038	2.761167
H	-3.463958	1.884230	-0.711888
H	-4.672098	1.490592	-2.838587
H	-3.737095	-0.072357	-4.531681
H	-1.587787	-1.242500	-4.092280
H	-0.373100	-0.858965	-1.975973
H	-0.047891	3.595287	-1.316244
H	-3.291773	-1.326249	1.437431
H	1.584653	5.205348	-2.268611
H	-4.087481	-3.400144	2.546614
H	4.017739	4.756372	-2.125013
H	-2.464863	-5.078609	3.378449
H	4.882866	2.709828	-1.027748
H	-0.022921	-4.732884	3.137168

Compound **4 neutral** - Etot(B3LYP/6-31+G*) = -2059.19193046 au

C	-4.442800	0.829293	2.374774
C	-3.305224	1.062274	1.612308
C	-2.207706	0.184314	1.718131
C	-2.297696	-0.918028	2.615305
C	-3.442845	-1.150691	3.382325
C	-4.514146	-0.269301	3.253143
C	-0.937408	0.206728	1.054383
C	-0.108864	-0.823489	1.433779
S	-0.819743	-1.888224	2.617338
C	1.198994	-0.823374	0.793889
S	2.569898	-1.887892	0.958937
C	3.475308	-0.917286	-0.208872
C	2.711505	0.184866	-0.688497
C	1.407791	0.206942	-0.093039
C	4.783805	-1.149588	-0.642098
C	5.339174	-0.268007	-1.567089
C	4.601664	0.830408	-2.049885
C	3.301404	1.063021	-1.619850
P	-0.094653	1.251338	-0.193384
C	-0.884112	0.905121	-1.806983
C	-1.267899	2.002899	-2.589030
C	-1.875881	1.796799	-3.831407
C	-2.101291	0.498298	-4.294007
C	-1.718742	-0.599576	-3.514385
C	-1.111847	-0.398156	-2.274469
O	0.035137	2.724675	0.072217
H	2.739739	1.917635	-1.986133
H	-3.249797	1.917023	0.944229
H	-1.893437	-1.610725	-3.872899
H	5.058722	1.507461	-2.766394
H	-1.086509	3.007464	-2.216806
H	5.356034	-1.993817	-0.267414
H	-0.816499	-1.254422	-1.672803
H	-3.498108	-1.995023	4.063945
H	6.355372	-0.430199	-1.915899
H	-2.574013	0.338813	-5.259894
H	-2.172016	2.650970	-4.435008
H	-5.413240	-0.431777	3.841245
H	-5.289128	1.506195	2.295898

Compound **4 radical anion** - Etot(B3LYP/6-31+G*) = -2059.24018384 au

C	-4.467432	0.778522	2.319001
C	-3.315813	1.012777	1.570318
C	-2.193882	0.159867	1.701988
C	-2.298020	-0.926494	2.630008
C	-3.448561	-1.156101	3.377077
C	-4.546704	-0.296790	3.219941
C	-0.926718	0.191285	1.055221
C	-0.057992	-0.850120	1.471156
S	-0.800971	-1.889133	2.688729
C	1.202248	-0.843490	0.851755
S	2.627731	-1.872792	1.001328
C	3.488929	-0.894943	-0.212158
C	2.682429	0.188191	-0.690286
C	1.395887	0.206038	-0.082217
C	4.785579	-1.111249	-0.666719
C	5.326317	-0.241272	-1.625596
C	4.556675	0.831281	-2.106852
C	3.258132	1.052066	-1.652420
P	-0.089264	1.230156	-0.160785
C	-0.895040	0.924541	-1.802145
C	-1.162167	2.014137	-2.641852
C	-1.757581	1.817452	-3.892989
C	-2.094149	0.527912	-4.313849
C	-1.832888	-0.565094	-3.478760
C	-1.237144	-0.366611	-2.231449
O	0.005888	2.731282	0.031865
H	2.680293	1.893790	-2.025104
H	-3.265357	1.856351	0.886729
H	-2.094450	-1.571349	-3.799979
H	4.982777	1.506930	-2.846480
H	-0.901112	3.010416	-2.294772
H	5.374342	-1.942485	-0.283783
H	-1.036334	-1.216329	-1.583182
H	-3.497386	-1.989225	4.075486
H	6.339260	-0.397946	-1.989081
H	-2.558453	0.373025	-5.285935
H	-1.960311	2.671617	-4.536657
H	-5.452190	-0.463763	3.798664
H	-5.320011	1.445761	2.205009

Compound **4 radical cation** - Etot(B3LYP/6-31+G*) = -2058.93494205 au

C	4.968827	0.322779	-0.937396
C	3.608839	0.572204	-1.001797
C	2.706963	-0.369017	-0.439943
C	3.227809	-1.557322	0.169593
C	4.593017	-1.802367	0.234390
C	5.456457	-0.850338	-0.324095
C	1.298309	-0.338982	-0.384656
C	0.749603	-1.485141	0.232858
S	1.942645	-2.612491	0.786104
C	-0.670713	-1.519658	0.250164
S	-1.793770	-2.703312	0.831586
C	-3.143294	-1.712160	0.247190
C	-2.695771	-0.500312	-0.374122
C	-1.289310	-0.401860	-0.353116
C	-4.493006	-2.023190	0.345048
C	-5.415006	-1.114547	-0.191680
C	-5.000004	0.080517	-0.815955
C	-3.655707	0.395669	-0.913286
P	-0.031202	0.796640	-0.971088
C	-0.053196	2.245826	0.112039
C	-0.091373	3.505820	-0.506093
C	-0.109795	4.659654	0.281243
C	-0.090303	4.557954	1.675069
C	-0.052238	3.301596	2.291615
C	-0.033612	2.144573	1.514010
O	-0.056485	1.102305	-2.434900
H	-3.327974	1.307472	-1.403244
H	3.225375	1.466715	-1.483107
H	-0.037164	3.225675	3.375074
H	-5.745293	0.754233	-1.226663
H	-0.106244	3.572815	-1.590277
H	-4.833304	-2.939993	0.816548
H	-0.004028	1.172467	2.001069
H	4.988820	-2.701270	0.696943
H	-6.475103	-1.342068	-0.127632
H	-0.104731	5.457549	2.284052
H	-0.139327	5.635443	-0.195029
H	6.527599	-1.026060	-0.285998
H	5.670295	1.031650	-1.365733

Compound **5 neutral** - Etot(B3LYP/6-31+G*) = -2382.15647622 au

C	-4.453558	0.690261	2.341762
C	-3.313290	0.923146	1.583178
C	-2.217970	0.043185	1.691504
C	-2.311971	-1.060793	2.585808
C	-3.460292	-1.293593	3.347870
C	-4.529757	-0.410255	3.217073
C	-0.946323	0.059078	1.030457
C	-0.119041	-0.973142	1.409682
S	-0.836113	-2.034827	2.592887
C	1.185818	-0.972567	0.772169
S	2.560602	-2.033382	0.933313
C	3.461363	-1.058389	-0.234998
C	2.697398	0.045279	-0.710038
C	1.394402	0.060113	-0.113132
C	4.768389	-1.290204	-0.672628
C	5.321899	-0.406177	-1.596357
C	4.583862	0.694046	-2.073770
C	3.284529	0.925951	-1.640353
P	-0.091465	1.128958	-0.186128
C	-0.886708	0.804762	-1.814140
C	-1.279312	1.880619	-2.617786
C	-1.884112	1.643185	-3.856146
C	-2.097358	0.334150	-4.293054
C	-1.705265	-0.743324	-3.490488
C	-1.101692	-0.510920	-2.254614
S	0.126797	3.034359	0.262313
H	2.722462	1.782318	-2.001351
H	-3.253220	1.779742	0.918168
H	-1.869576	-1.763623	-3.827166
H	5.039470	1.373335	-2.789053
H	-1.108748	2.895298	-2.268333
H	5.340779	-2.136156	-0.302097
H	-0.799658	-1.352389	-1.636401
H	-3.519195	-2.139780	4.026883
H	6.337082	-0.567994	-1.948274
H	-2.567578	0.150903	-5.255875
H	-2.187049	2.482986	-4.476172
H	-5.431156	-0.572849	3.801601
H	-5.298285	1.368996	2.261782

Compound **5 radical anion** - Etot(B3LYP/6-31+G*) = -2382.20621888 au

C	-4.453513	0.646652	2.358936
C	-3.308738	0.882297	1.600062
C	-2.199756	0.009421	1.697717
C	-2.305699	-1.096154	2.601108
C	-3.450637	-1.328449	3.356117
C	-4.537418	-0.449800	3.233202
C	-0.941873	0.030692	1.032240
C	-0.076878	-1.025422	1.418692
S	-0.821192	-2.080408	2.620957
C	1.180902	-1.007904	0.798534
S	2.605140	-2.042020	0.917247
C	3.473438	-1.020248	-0.254442
C	2.672570	0.080108	-0.698774
C	1.381287	0.070237	-0.100385
C	4.773011	-1.221123	-0.708132
C	5.320530	-0.315882	-1.629163
C	4.556322	0.776022	-2.073673
C	3.254260	0.980609	-1.621768
P	-0.098316	1.102042	-0.147502
C	-0.906124	0.819659	-1.802073
C	-1.016123	1.851170	-2.742015
C	-1.587824	1.609364	-3.995672
C	-2.061256	0.334734	-4.318399
C	-1.958834	-0.699364	-3.381058
C	-1.382878	-0.458933	-2.131879
S	0.061465	3.068707	0.206010
H	2.680621	1.838512	-1.961685
H	-3.251831	1.742838	0.938992
H	-2.329688	-1.693554	-3.621773
H	4.989256	1.479923	-2.782139
H	-0.661960	2.842998	-2.473045
H	5.358342	-2.066709	-0.352553
H	-1.305592	-1.263362	-1.405023
H	-3.502682	-2.177119	4.035197
H	6.335671	-0.460084	-1.991604
H	-2.510071	0.147308	-5.291908
H	-1.667716	2.420404	-4.717041
H	-5.438102	-0.618013	3.818961
H	-5.296745	1.329638	2.273687

Compound **5 radical cation** - Etot(B3LYP/6-31+G*) = -2381.90023558 au

C	-4.971440	0.384520	0.727868
C	-3.609258	0.622975	0.793881
C	-2.710411	-0.372871	0.333836
C	-3.236314	-1.602958	-0.177302
C	-4.603995	-1.838010	-0.243786
C	-5.464789	-0.832522	0.213309
C	-1.298291	-0.364025	0.287941
C	-0.756521	-1.563639	-0.225135
S	-1.958601	-2.722885	-0.685857
C	0.661145	-1.602123	-0.253041
S	1.779542	-2.824343	-0.759495
C	3.135115	-1.775971	-0.302606
C	2.697205	-0.519692	0.227439
C	1.286933	-0.434211	0.237056
C	4.484364	-2.084818	-0.422469
C	5.415725	-1.127997	-0.000612
C	5.009719	0.113481	0.531599
C	3.666127	0.425429	0.650774
P	0.037445	0.783017	0.822761
C	0.053337	2.197460	-0.322132
C	0.098987	3.496925	0.201943
C	0.111632	4.591339	-0.666302
C	0.078943	4.390486	-2.048676
C	0.033356	3.092892	-2.572352
C	0.020427	1.994960	-1.713669
S	0.085698	1.169588	2.742309
H	3.347982	1.373458	1.073412
H	-3.223796	1.551891	1.202699
H	0.007990	2.938319	-3.647209
H	5.761301	0.826677	0.855001
H	0.124212	3.645269	1.277855
H	4.815598	-3.036485	-0.826620
H	-0.015051	0.990720	-2.129153
H	-5.001989	-2.769879	-0.633589
H	6.475160	-1.352771	-0.082352
H	0.088908	5.244018	-2.720733
H	0.146987	5.598299	-0.260687
H	-6.537250	-0.999401	0.173477
H	-5.669939	1.137095	1.079776

Compound **B1 neutral** Etot(B3LYP/6-31+G*) = -1676.63412073 au

P	-0.343054	0.000000	1.446111
C	1.513452	0.000000	1.446111
C	2.164412	0.000000	2.688305
C	3.562467	0.000000	2.759984
C	4.320162	0.000000	1.588030
C	3.678423	0.000000	0.343149
C	2.285335	0.000000	0.272213
H	1.793820	0.000000	-0.697261
H	4.265655	0.000000	-0.571954
H	5.406072	0.000000	1.640293
H	4.053985	0.000000	3.729717
H	1.576685	0.000000	3.603520
C	-0.784377	1.287812	0.209017
C	-0.784377	-1.287812	0.209017
C	-1.354980	0.721263	-0.923995
C	-1.354980	-0.721263	-0.923995
S	-1.917792	1.926736	-2.039581
S	-1.917792	-1.926736	-2.039581
C	-1.375086	3.199867	-0.972368
C	-1.375086	-3.199867	-0.972368
C	-0.807310	2.712671	0.177856
C	-0.807310	-2.712671	0.177856
H	-0.418884	3.352981	0.963038
H	-0.418884	-3.352981	0.963038
H	-1.513888	4.232915	-1.264174
H	-1.513888	-4.232915	-1.264174

Compound **B1 radical anion** - Etot(B3LYP/6-31+G*) = -1676.64694459 au

C	0.704576	-0.686291	-2.724476
C	0.686143	-0.562156	-1.316037
C	-0.069010	-1.595614	-0.686804
S	-0.766018	-2.687905	-1.882592
C	-0.027755	-1.754638	-3.204040
P	1.485926	0.521189	-0.077728
C	0.770502	-0.516503	1.253327
C	-0.031445	-1.563689	0.714772
S	-0.674432	-2.589321	1.995743
C	0.143374	-1.606155	3.229444
C	0.861398	-0.571320	2.662015
C	0.350471	2.041722	-0.062899
C	0.854682	3.239760	0.463538
C	0.064567	4.393298	0.528074

C	-1.252242	4.363107	0.058964
C	-1.765437	3.175343	-0.476775
C	-0.969792	2.028115	-0.541923
H	-1.367198	1.109580	-0.966916
H	-2.790142	3.144179	-0.844958
H	-1.872175	5.256869	0.105227
H	0.478643	5.314806	0.936103
H	1.883733	3.269320	0.822524
H	1.433660	0.132965	3.261996
H	1.234491	-0.004978	-3.386821
H	0.035827	-1.861980	4.275608
H	-0.198722	-2.052863	-4.230331

Compound **B1 radical cation** - Etot(B3LYP/6-31+G*) = -1676.37569997 au

P	-0.288241	0.000000	1.451806
C	1.550369	0.000000	1.451806
C	2.179560	0.000000	2.707778
C	3.574906	0.000000	2.791353
C	4.344311	0.000000	1.625638
C	3.722072	0.000000	0.371122
C	2.330960	0.000000	0.280955
H	1.858589	0.000000	-0.698160
H	4.322013	0.000000	-0.534607
H	5.428646	0.000000	1.691450
H	4.056465	0.000000	3.764911
H	1.584042	0.000000	3.617242
C	-0.760306	1.273584	0.204076
C	-0.760306	-1.273584	0.204076
C	-1.401889	0.699121	-0.938233
C	-1.401889	-0.699121	-0.938233
S	-1.999317	1.912093	-2.040231
S	-1.999317	-1.912093	-2.040231
C	-1.374929	3.152639	-0.997384
C	-1.374929	-3.152639	-0.997384
C	-0.753422	2.671722	0.151659
C	-0.753422	-2.671722	0.151659
H	-0.328466	3.325627	0.905055
H	-0.328466	-3.325627	0.905055
H	-1.508793	4.191697	-1.276998
H	-1.508793	-4.191697	-1.276998

Compound **B2 neutral** - Etot(B3LYP/6-31+G*) = -1751.88052640 au

C	0.474916	-0.663449	-2.728932
C	0.500298	-0.608454	-1.308508
C	-0.148632	-1.677564	-0.714545
S	-0.799659	-2.767587	-1.889967
C	-0.192046	-1.772199	-3.189227
P	1.182170	0.503261	-0.019327
C	0.535663	-0.591109	1.302478
C	-0.128928	-1.667895	0.740562
S	-0.747829	-2.741998	1.947570
C	-0.105525	-1.729486	3.216560
C	0.548631	-0.627133	2.723677
C	0.162889	2.022183	-0.015658
C	0.834629	3.251870	-0.032545
C	0.106329	4.445683	-0.030652
C	-1.289976	4.414392	-0.011950
C	-1.963096	3.187055	0.004943
C	-1.240030	1.993820	0.003113
H	-1.767858	1.043140	0.016277
H	-3.049699	3.160935	0.019515
H	-1.855461	5.342889	-0.010497
H	0.631277	5.397466	-0.043798
H	1.920955	3.260609	-0.047013
H	1.023072	0.116234	3.355014
H	0.931971	0.071366	-3.382710
H	-0.247372	-2.018678	4.249848
H	-0.361699	-2.075112	-4.214360
O	2.653918	0.804914	-0.041242

Compound **B2 radical anion** - Etot(B3LYP/6-31+G*) = -1751.91279321 au

C	0.492479	-0.629094	-2.701144
C	0.509975	-0.591955	-1.285478
C	-0.149967	-1.712642	-0.699731
S	-0.762985	-2.799685	-1.939480
C	-0.147341	-1.732018	-3.218479
P	1.173243	0.476422	0.004918
C	0.506431	-0.591509	1.294573
C	-0.149340	-1.713846	0.706728
S	-0.756104	-2.806276	1.944940
C	-0.141935	-1.739870	3.225996
C	0.492986	-0.633289	2.710226
C	0.175068	2.044072	0.006389
C	0.832365	3.275928	-0.116195

C	0.105970	4.472488	-0.133115
C	-1.287483	4.448305	-0.024438
C	-1.951463	3.221622	0.101631
C	-1.224019	2.029359	0.116699
H	-1.740103	1.077162	0.215146
H	-3.036177	3.195642	0.188315
H	-1.854360	5.377574	-0.036270
H	0.628808	5.422920	-0.228279
H	1.916659	3.275256	-0.191112
H	0.945539	0.125877	3.343333
H	0.946693	0.130013	-3.333082
H	-0.284881	-2.015551	4.262883
H	-0.290464	-2.005946	-4.255813
O	2.636588	0.885097	-0.003528

Compound **B2 radical cation** - Etot(B3LYP/6-31+G*) = -1751.60952269 au

C	0.444962	-0.652005	-2.690644
C	0.446945	-0.577796	-1.297570
C	-0.156170	-1.717128	-0.691470
S	-0.729351	-2.857750	-1.871124
C	-0.159136	-1.824326	-3.143243
P	1.123847	0.576268	-0.019265
C	0.482665	-0.560777	1.292302
C	-0.136712	-1.707864	0.718081
S	-0.677046	-2.832728	1.927985
C	-0.072129	-1.782811	3.170209
C	0.519037	-0.616640	2.685761
C	0.134678	2.083597	-0.015462
C	0.833111	3.301923	-0.034860
C	0.119776	4.502422	-0.033057
C	-1.277970	4.487931	-0.012074
C	-1.974099	3.272955	0.007300
C	-1.271932	2.069158	0.005688
H	-1.820421	1.129767	0.020847
H	-3.060062	3.266601	0.023601
H	-1.828631	5.424377	-0.010743
H	0.656246	5.446596	-0.048005
H	1.919139	3.300152	-0.050950
H	0.953333	0.137000	3.333195
H	0.861105	0.092985	-3.359650
H	-0.179132	-2.078123	4.208145
H	-0.294629	-2.133255	-4.173861
O	2.604942	0.768212	-0.041142

Compound **B3 neutral** - Etot(B3LYP/6-31+G*) = -2074.84511847 au

C	0.302397	-0.697517	-2.721335
C	0.313435	-0.645567	-1.301280
C	-0.355717	-1.704303	-0.710532
S	-1.013385	-2.782865	-1.893933
C	-0.380200	-1.793949	-3.186651
P	1.030743	0.445291	-0.014175
C	0.342513	-0.628193	1.303016
C	-0.339492	-1.694612	0.741472
S	-0.971159	-2.756774	1.953522
C	-0.309737	-1.750661	3.218543
C	0.362533	-0.660861	2.723560
C	0.021261	1.984631	-0.013240
C	0.659673	3.229356	-0.034608
C	-0.099311	4.403929	-0.034832
C	-1.493979	4.337971	-0.013739
C	-2.134596	3.093668	0.007695
C	-1.381237	1.919579	0.007976
H	-1.884826	0.956402	0.024623
H	-3.220030	3.038364	0.024180
H	-2.082864	5.251741	-0.013894
H	0.402462	5.367983	-0.051436
H	1.745391	3.269775	-0.050664
H	0.854660	0.074650	3.350297
H	0.780397	0.029478	-3.368606
H	-0.455141	-2.034579	4.252789
H	-0.548307	-2.091761	-4.213522
S	2.978409	0.733249	-0.038176

Compound **B3 radical anion** - Etot(B3LYP/6-31+G*) = -2074.87993432 au

C	0.460120	-0.637401	-2.685375
C	0.385838	-0.617704	-1.271573
C	-0.351824	-1.714399	-0.739194
S	-0.939457	-2.754440	-2.029261
C	-0.196675	-1.703911	-3.252286
P	1.019520	0.406158	0.066739
C	0.263042	-0.661724	1.303994
C	-0.408773	-1.744937	0.664829
S	-1.075824	-2.853211	1.856334
C	-0.445749	-1.853061	3.181822
C	0.235009	-0.752505	2.717142
C	0.040760	1.993457	0.059431
C	0.613475	3.195976	-0.377074

C	-0.148983	4.366401	-0.436186
C	-1.493315	4.351456	-0.050171
C	-2.070099	3.156099	0.392853
C	-1.309983	1.984810	0.444257
H	-1.760703	1.057122	0.786818
H	-3.114141	3.134907	0.699829
H	-2.085865	5.263580	-0.090108
H	0.311148	5.293302	-0.774341
H	1.666099	3.204123	-0.648080
H	0.707780	-0.032974	3.380192
H	0.991650	0.104529	-3.275000
H	-0.622233	-2.154640	4.206158
H	-0.290309	-1.958809	-4.299977
S	2.981951	0.846473	0.129090

Compound **B3 radical cation** - Etot(B3LYP/6-31+G*) = -2074.57700845 au

C	0.239244	-0.657236	-2.694138
C	0.245318	-0.602154	-1.293629
C	-0.302948	-1.768805	-0.695055
S	-0.840790	-2.910438	-1.884091
C	-0.323402	-1.838475	-3.153195
P	0.902535	0.531866	-0.009162
C	0.264641	-0.588755	1.296709
C	-0.292017	-1.761477	0.718611
S	-0.810550	-2.891361	1.927430
C	-0.274259	-1.806671	3.177353
C	0.280504	-0.629753	2.697620
C	-0.043528	2.075444	-0.007127
C	0.644277	3.297098	-0.059724
C	-0.077635	4.492598	-0.062974
C	-1.473754	4.469208	-0.014023
C	-2.159980	3.249240	0.038953
C	-1.450191	2.050638	0.042771
H	-1.990385	1.107789	0.085013
H	-3.245274	3.234534	0.077545
H	-2.031165	5.401597	-0.016476
H	0.452594	5.439461	-0.103170
H	1.729755	3.309053	-0.095843
H	0.668732	0.149267	3.343921
H	0.617568	0.115087	-3.354189
H	-0.404843	-2.093825	4.214393
H	-0.470460	-2.135935	-4.185115
S	2.869088	0.652110	-0.029570

Compound **B4 closed shell cation** - Etot(B3LYP/6-31+G*) = -1716.33268431 au

P	0.405707	0.000000	0.975230
C	0.405707	0.000000	2.796813
C	2.090514	0.000000	0.330485
C	3.199237	0.000000	1.192811
C	4.489380	0.000000	0.657811
C	4.673749	0.000000	-0.726590
C	3.568992	0.000000	-1.586338
C	2.277626	0.000000	-1.064193
H	1.423751	0.000000	-1.736743
H	3.714258	0.000000	-2.662469
H	5.678882	0.000000	-1.138272
H	5.346491	0.000000	1.324551
H	3.073338	0.000000	2.271102
C	-0.641548	1.311477	0.316798
C	-0.641548	-1.311477	0.316798
C	-1.726996	0.727211	-0.329702
C	-1.726996	-0.727211	-0.329702
S	-2.788178	1.922459	-0.970419
S	-2.788178	-1.922459	-0.970419
C	-1.768602	3.201866	-0.370693
C	-1.768602	-3.201866	-0.370693
C	-0.661744	2.733410	0.292811
C	-0.661744	-2.733410	0.292811
H	0.090012	3.381642	0.728772
H	0.090012	-3.381642	0.728772
H	-2.051228	4.231335	-0.549633
H	-2.051228	-4.231335	-0.549633
H	-0.634655	0.000000	3.133820
H	0.905944	-0.894540	3.179666
H	0.905944	0.894540	3.179666

Compound **B4 radical neutral** - Etot(B3LYP/6-31+G*) = -1716.49408454 au

P	0.287466	0.000000	0.998301
C	0.287466	0.000000	2.845686
C	2.068546	0.000000	0.525420
C	3.117135	0.000000	1.457352
C	4.446585	0.000000	1.022693
C	4.736710	0.000000	-0.343050
C	3.695412	0.000000	-1.277907
C	2.369311	0.000000	-0.847026
H	1.560687	0.000000	-1.573588
H	3.916926	0.000000	-2.341862

H	5.770245	0.000000	-0.679591
H	5.251921	0.000000	1.752801
H	2.912081	0.000000	2.523398
C	-0.676555	1.291791	0.280537
C	-0.676555	-1.291791	0.280537
C	-1.739201	0.703097	-0.476396
C	-1.739201	-0.703097	-0.476396
S	-2.727180	1.943900	-1.214378
S	-2.727180	-1.943900	-1.214378
C	-1.712419	3.214598	-0.518888
C	-1.712419	-3.214598	-0.518888
C	-0.684449	2.717145	0.233762
C	-0.684449	-2.717145	0.233762
H	0.038558	3.356122	0.732088
H	0.038558	-3.356122	0.732088
H	-1.954633	4.250396	-0.716302
H	-1.954633	-4.250396	-0.716302
H	-0.758045	0.000000	3.164131
H	0.780309	-0.895226	3.240754
H	0.780309	0.895226	3.240754

Close shell cation of 8 - Etot(B3LYP/6-31+G*) = -2023.64551773 au

C	0.043944	2.286693	-1.469092
C	-0.304986	2.277622	-0.106350
C	-0.643726	3.475545	0.543897
C	-0.632247	4.676040	-0.170040
C	-0.285541	4.683344	-1.522981
C	0.052131	3.489743	-2.171435
P	-0.304030	0.700288	0.772244
C	-0.792517	0.931522	2.512643
C	-1.278867	-0.589909	-0.017226
C	-2.645519	-0.809469	-0.394495
C	-2.792138	-2.102055	-0.974185
S	-1.262279	-2.985997	-1.038476
C	-0.439239	-1.653024	-0.301865
C	-3.780920	0.017834	-0.284483
C	-5.008558	-0.447655	-0.736357
C	-5.133903	-1.731238	-1.302605
C	-4.029280	-2.568817	-1.428033
C	0.954704	-1.449669	0.062645
C	1.234857	-0.223204	0.640119
C	2.616424	-0.041899	0.981669
C	3.363236	-1.204188	0.635716
S	2.352735	-2.458690	-0.093007

C	3.290655	1.049376	1.564942
C	4.657743	0.962357	1.791769
C	5.377910	-0.197923	1.446736
C	4.739560	-1.289744	0.865452
H	-0.915713	3.487640	1.594997
H	-0.894307	5.602003	0.333203
H	-0.277924	5.619149	-2.074389
H	0.321483	3.496573	-3.223383
H	0.306906	1.362887	-1.977911
H	2.749455	1.954725	1.827248
H	-3.697110	1.014307	0.141401
H	5.181279	1.801676	2.239824
H	-5.885714	0.187338	-0.654617
H	6.446469	-0.242638	1.634314
H	-6.104638	-2.073404	-1.648438
H	5.298172	-2.181876	0.598135
H	-4.128765	-3.556929	-1.867515
H	-0.777439	-0.048464	2.997764
H	-0.088404	1.594040	3.024553
H	-1.802948	1.345943	2.576251

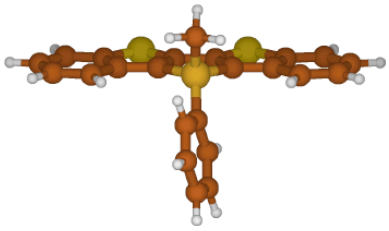
Neutralized cation of 8 (radical) - Etot(B3LYP/6-31+G*) = -2023.81413085 au

C	-0.495777	2.264909	-1.489738
C	-0.366151	2.269374	-0.091030
C	-0.210104	3.492034	0.581495
C	-0.185294	4.691252	-0.135350
C	-0.319603	4.679424	-1.525946
C	-0.477345	3.464654	-2.201140
P	-0.314494	0.652992	0.778181
C	-0.821853	1.019434	2.513361
C	-1.250448	-0.607862	-0.026513
C	-2.606657	-0.830021	-0.433893
C	-2.757415	-2.112428	-1.039696
S	-1.228474	-3.021971	-1.092051
C	-0.380481	-1.698879	-0.313452
C	-3.747457	-0.008193	-0.333692
C	-4.975718	-0.456239	-0.817637
C	-5.101412	-1.723056	-1.407567
C	-3.985733	-2.559368	-1.521061
C	0.956724	-1.494336	0.064542
C	1.208639	-0.242142	0.692467
C	2.583719	-0.039665	1.041091
C	3.375696	-1.171453	0.685711
S	2.415986	-2.456389	-0.084307

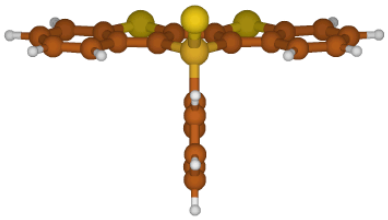
C	3.231666	1.054224	1.649864
C	4.603017	1.006905	1.894626
C	5.361101	-0.120200	1.542601
C	4.745878	-1.218276	0.932656
H	-0.111925	3.522427	1.662827
H	-0.064056	5.632721	0.394170
H	-0.302600	5.613243	-2.081758
H	-0.587070	3.450944	-3.282220
H	-0.618142	1.320938	-2.014230
H	2.663392	1.940840	1.922095
H	-3.668097	0.979127	0.115653
H	5.091266	1.857723	2.363362
H	-5.848185	0.187232	-0.735717
H	6.429141	-0.142620	1.740442
H	-6.065863	-2.058949	-1.778189
H	5.329204	-2.092214	0.654023
H	-4.077418	-3.541466	-1.977987
H	-0.923094	0.062280	3.031541
H	-0.060296	1.615426	3.026988
H	-1.779001	1.550674	2.537825

4) Simulated UV spectra and NCIS values for compounds 3, 4, 5, and 8.

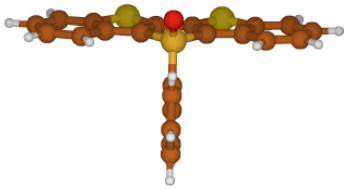
Figure S4. B3LYP/6-31G* optimized structures of the benzoannelated species BSP(Ph,E)SB



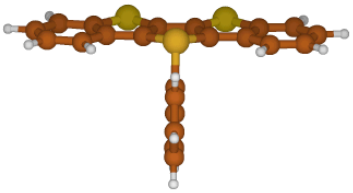
E = Me^+



E = S



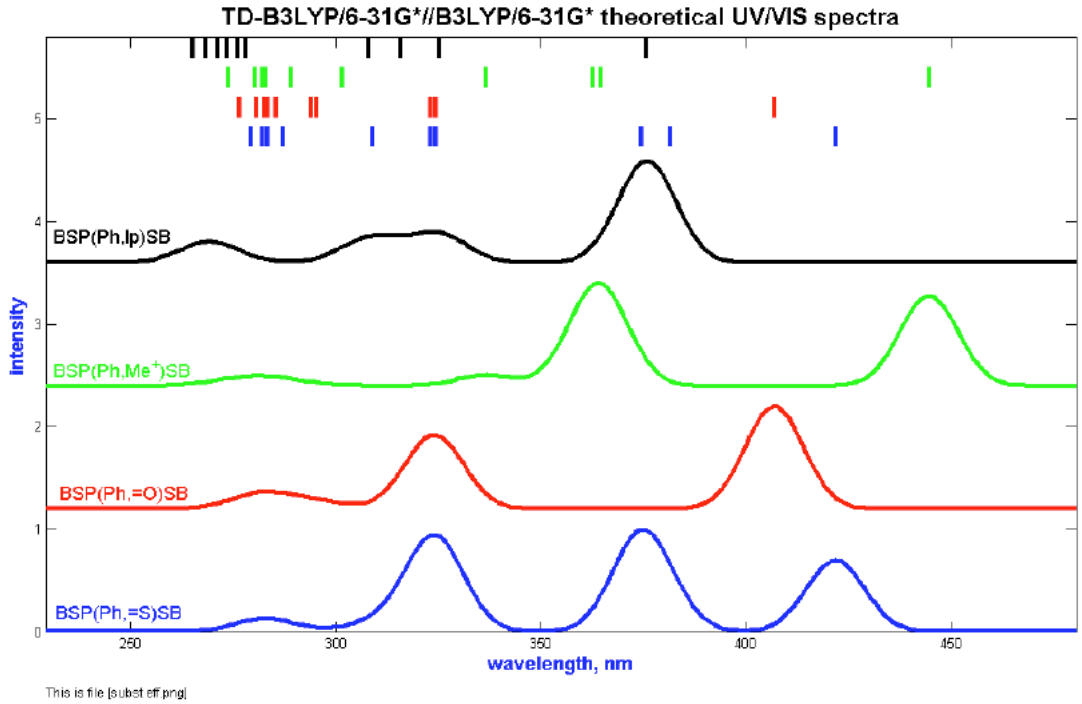
E = O



E = lp

(B=phenyl, Ph=P-phenyl, S=thienyl, P=phosphole, E=Me^+, S, O, lp)

Figure S5. TD-B3LYP/6-31G*//B3LYP/6-31G* theoretical UV spectra of the BSP(Ph,E)SB species



(B=phenyl, Ph=P-phenyl, S=thienyl, P=phosphole, E=Me^+, S, O, lp)

Table S1. Simulated UV/Vis data for the DFT-optimized (gaseous phase) structure of **3**.

Band	Position		Pole strength
	nm	eV	
1	375.84	3.30	0.3892
2	325.11	3.81	0.1067
3	315.66	3.93	0.0107
4	307.97	4.03	0.0894
5	278.10	4.46	0.0007
6	276.03	4.49	0.0013
7	273.39	4.54	0.0030
8	271.18	4.57	0.0281
9	268.12	4.62	0.0434
10	265.15	4.68	0.0079

Table S2. Simulated UV/Vis data for the DFT-optimized (gaseous phase) structure of **4**.

Band	Position		Pole strength
	nm	eV	
1	407.00	3.05	0.2899
2	324.43	3.82	0.1440
3	323.01	3.84	0.0663
4	295.14	4.20	0.0167
5	293.99	4.22	0.0065
6	285.38	4.34	0.0013
7	283.37	4.38	0.0069
8	282.63	4.39	0.0086
9	280.57	4.42	0.0269
10	276.46	4.48	0.0002

Table S3. Simulated UV/Vis data for the DFT-optimized (gaseous phase) structure of **5**.

Band	Position		Pole strength
	nm	eV	
1	421.88	2.94	0.1348
2	381.73	3.25	0.0163
3	374.51	3.31	0.1836
4	324.41	3.82	0.1180
5	323.23	3.84	0.0645
6	308.93	4.01	0.0152
7	287.21	4.32	0.0029
8	283.38	4.38	0.0056
9	282.15	4.39	0.0161
10	279.32	4.44	0.0012

Table S4. Simulated UV/Vis data for the DFT-optimized (gaseous phase) structure of **5**.

Band	Position		Pole strength
	nm	eV	
1	444.69	2.79	0.2009
2	364.74	3.40	0.1477
3	362.53	3.42	0.0838
4	336.51	3.68	0.0237
5	301.52	4.11	0.0005
6	289.21	4.29	0.0067
7	282.75	4.38	0.0087
8	282.03	4.40	0.0031
9	280.41	4.42	0.0016
10	273.70	4.53	0.0094

Table S5. GIAO-HF/6-31G*//Becke3LYP/6-31G* NICS data for the each ring of the studied species

P-substituent	[1] Ring	[2] $NICS_{-2}$	$NICS_{-1}$	$NICS_{0}$	$NICS_{+1}$	$NICS_{+2}$
[3] Me^{+}	P	+0.03	+2.12	+3.57	+1.29	+0.65
	S	-3.25 / -3.71	-7.89 / -8.25	-9.42 / -9.80	-8.02 / -8.28	-3.55 / -3.67
	B	-12.99 / -13.15	-5.59 / -5.85	-12.10 / -12.19	-12.92 / -12.95	-5.58 / -5.60
	Ph	-5.18 / -5.39	-12.35 / -12.28	-10.48	–	–
O	P	-0.47	+2.29	+4.74	+2.61	+0.08
	S	-3.56	-8.16	-9.59	-8.03	-3.46
	B	-5.83	-13.02	-12.11	-12.87	-5.52
	Ph	-5.53	-12.68	-11.03	–	–
S	P	-1.27	+1.57	+3.2	+1.00	-0.65
	S	-3.57	-8.07	-9.72	-8.13	-3.56
	B	-5.89	-13.09	-12.17	-12.93	-5.56
	Ph	-5.69	-12.81	-11.09	–	–
(none)	P	-1.45	-0.63	-0.16	-2.00	-1.75
	S	-3.37	-7.54	-8.86	-7.82	-3.60
	B	-5.68	-12.83	-11.96	-12.77	-5.51
	Ph	-5.35	-12.45	-10.73	–	–

[1]P: phosphole, S: thiophene, B: phenyl, Ph: P-Phenyl
[2]$NICS_z$: z>0 at the half-space containing the P-substituent [ppm]
[3]NICS data reflects that this species does not have the C_s symmetry.

Table S6. Reference data for the monocyclic fragments (GIAO-HF/6-31G*//-Becke3LYP/6-31G*)

Species	$NICS_{-2}$	$NICS_{-1}$	$NICS_{0}$	$NICS_{+1}$	$NICS_{+2}$
benzene	–	–	-11.54	-12.81	-5.46
thiophene	–	–	-14.27	-11.14	-4.42
[1] phosphole	-2.52	-5.42	-5.60	-5.64	-2.74

[2]$NICS_z$: z>0 at the half-space containing the P-hydrogen atom [ppm]