

# Supporting Information for:

## Restriction of Flip-Flop Motion as A Mechanism for Aggregation-Induced Emission

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### Computational Details:

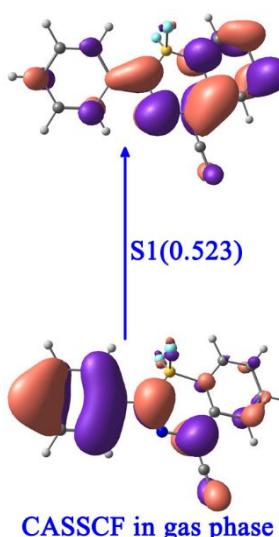
All the DFT and TDDFT calculations in this work were carried out with Gaussian 16 software.<sup>S1</sup> The TZVP basis set was adopted and solvent effects were included by the integral equation formalism version<sup>S2,S3</sup> of the polarizable continuum model (IEFPCM).<sup>S4,S5</sup> The S<sub>0</sub> and S<sub>1</sub> geometries of BODIHY derivatives were optimized using DFT and TDDFT methods with B3LYP and CAM-B3LYP functionals, respectively. We have also optimized the S<sub>0</sub> geometries of compound **1** with PBE, and we found that the optimized geometry is essentially identical to that of B3LYP. The TDA-PBE and TDA-PBE computed VEEs at the PBE optimized S<sub>0</sub> geometry are also essentially identical to those of computed values at the B3LYP optimized S<sub>0</sub> geometry. Therefore, the reported VEEs by TDA-PBE and TD-PBE in this study were based on the B3LYP optimized geometries.

All the SA2-CASSCF and XMCQDPT2 calculations were performed in gas

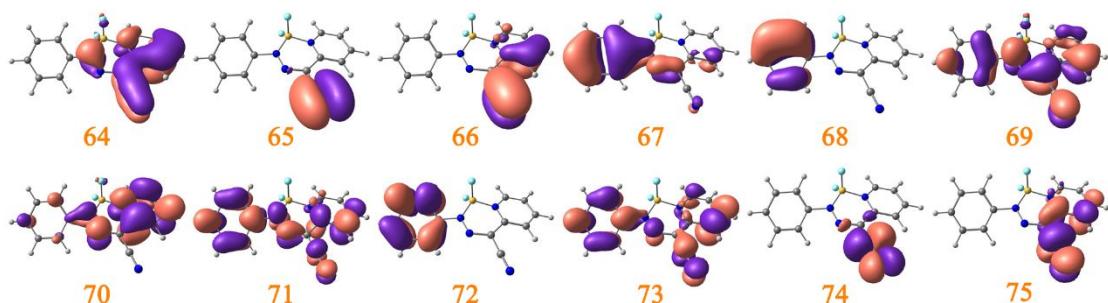
phase and carried out with Firefly 8.1.1 package.<sup>S6</sup> The active space comprises  $12\pi$  electrons in  $12\pi$  orbitals and the 6-31g(d) basis set was adopted. The geometries were optimized at the SA2-CASSCF level and the energies were corrected by the XMCQDPT2<sup>S7</sup> method to include dynamical correlation effects, where the intruder state avoidance was set to 0.02. The MECIs were located at the SA2-CASSCF level by using the Lagrange multiplier technique with semi-numerical state-specific gradients for SA-CASSCF. The LIIC pathways between the S<sub>1</sub>-min (or S<sub>0</sub>-min) and MECI were constructed and the energy profiles were calculated at the XMCQDPT2 level. For all the optimized geometries, frequency calculation was performed at the same level to confirm that each optimized geometry corresponds to a real minimum without negative frequency.

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- S7. Granovsky, A. A. Extended Multi-Configuration Quasi-Degenerate Perturbation Theory: The New Approach to Multi-State Multi-Reference Perturbation theory. *J. Chem. Phys.* **2011**, *134*, No. 214113.



**Figure S1.** The computed molecular orbitals involved in S<sub>1</sub> state of compound 1 by SA2-CASSCF method in gas phase.



**Figure S2.** Orbitals involved in the (12,12) active space optimized for the compound 1.

### B3LYP/TZVP optimized S<sub>0</sub>-min geometry of compound 1

F	0.333075000	-2.136153000	-0.676275000
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F	-0.046373000	-1.690843000	1.537467000
B	-0.110507000	-1.186526000	0.234001000
N	0.698361000	0.137001000	0.114970000
N	0.162619000	1.324625000	0.196491000
N	-1.625565000	-0.848681000	-0.080209000
N	-1.981933000	3.903386000	0.453158000
C	-1.145210000	1.474554000	0.207546000
C	-2.110293000	0.416091000	0.010413000
C	-3.481434000	0.646601000	-0.155286000
H	-3.860472000	1.655589000	-0.082394000
C	-4.325920000	-0.410738000	-0.420584000
H	-5.386033000	-0.237880000	-0.548755000
C	-3.802856000	-1.702282000	-0.530318000
H	-4.434167000	-2.552323000	-0.743094000
C	-2.453579000	-1.884238000	-0.352813000
H	-1.985510000	-2.855064000	-0.415051000
C	-1.598115000	2.819790000	0.340228000
C	2.121806000	0.125674000	-0.019291000
C	2.864787000	-0.933775000	0.507003000
H	2.372108000	-1.737309000	1.035237000
C	4.248397000	-0.939775000	0.370573000
H	4.817789000	-1.761340000	0.786862000
C	4.899944000	0.101642000	-0.283762000
H	5.977665000	0.092008000	-0.386089000
C	4.154410000	1.154739000	-0.808342000
H	4.649624000	1.965740000	-1.327691000
C	2.770887000	1.167606000	-0.686141000
H	2.189890000	1.976529000	-1.105972000

### B3LYP/TZVP optimized S<sub>1</sub>-min geometry of compound 1

F	0.176292000	-1.946711000	-1.145241000
F	0.176401000	-1.947101000	1.145662000
B	-0.112599000	-1.197020000	0.000352000
N	0.731600000	0.127874000	0.000501000
N	0.189478000	1.402638000	0.000858000
N	-1.635726000	-0.857060000	0.000419000
N	-1.972207000	3.936913000	0.000293000
C	-1.128732000	1.492526000	0.000232000
C	-2.103370000	0.440913000	-0.000289000
C	-3.490251000	0.670639000	-0.001072000
H	-3.853041000	1.689020000	-0.001721000
C	-4.373428000	-0.384609000	-0.001001000
H	-5.439344000	-0.203504000	-0.001599000

C	-3.869029000	-1.704654000	-0.000120000
H	-4.527272000	-2.561016000	0.000037000
C	-2.512458000	-1.893428000	0.000518000
H	-2.070733000	-2.879499000	0.001098000
C	-1.598706000	2.843750000	0.000256000
C	2.093837000	0.114624000	0.000285000
C	2.813778000	-1.123786000	0.000007000
H	2.277988000	-2.058682000	0.000243000
C	4.187100000	-1.124244000	-0.000635000
H	4.716499000	-2.068156000	-0.000873000
C	4.911031000	0.079915000	-0.000846000
H	5.992906000	0.063152000	-0.001402000
C	4.223397000	1.299423000	-0.000345000
H	4.778090000	2.228932000	-0.000370000
C	2.847623000	1.334738000	0.000307000
H	2.316895000	2.271771000	0.000751000

**SA2-CASSCF(12,12) optimized S<sub>0</sub>-min geometry of compound 1 (Because the state-specific gradients for state-averaged CASSCF in Firefly is computed in a seminumeric way, a very small imaginary frequency (22.43I) is obtained in the frequency calculation on this geometry even if we have increased the overall precision of computations as proposed in the Firefly documentation. The small imaginary frequency was verified to be a combination of translational and rotational motion.)**

F	0.208456410	-2.037417456	-0.905044476
F	0.075401094	-1.813481451	1.336483687
B	-0.102570778	-1.202081740	0.128617284
N	0.707065868	0.127776020	0.044696757
N	0.172470389	1.305965513	0.043969652
N	-1.634824946	-0.820927086	-0.004732565
N	-2.024174756	3.915007176	0.064495919
C	-1.135772056	1.472015387	0.049066207
C	-2.075007605	0.412993740	-0.001461950
C	-3.495969284	0.650805470	-0.070009206
C	-4.335575860	-0.406128433	-0.143892981
C	-3.818923381	-1.736288514	-0.154398793
C	-2.490854921	-1.893397552	-0.085076634
C	-1.597577643	2.836098663	0.057585432
C	2.117322218	0.126796335	0.003050685
C	2.828749723	-1.076211871	0.175127309
C	4.211075404	-1.066085245	0.129642760
C	4.916781282	0.128312118	-0.084102460
C	4.219255603	1.301481554	-0.249296398

C	2.832459902	1.321169377	-0.209758510
H	4.745791114	2.224469272	-0.413526737
H	-3.850856107	1.661304856	-0.063936712
H	-5.396616838	-0.244488504	-0.197507098
H	-4.469339846	-2.586339197	-0.214265211
H	-2.011192763	-2.849554338	-0.087081085
H	2.313166942	-1.997332986	0.347368880
H	4.746403231	-1.988207491	0.264859955
H	5.990943549	0.121103994	-0.116084323
H	2.302780784	2.241215607	-0.338964028

### SA2-CASSCF(12,12) optimized S<sub>1</sub>-min geometry of compound 1

F	0.197870853	-1.986868027	-1.045631903
F	0.180974844	-1.908654168	1.208855218
B	-0.107514645	-1.226409014	0.054383771
N	0.727928512	0.111796417	0.014435380
N	0.166272440	1.399773757	-0.029358278
N	-1.613530278	-0.870746922	0.030270675
N	-2.017007253	3.922838925	-0.122099965
C	-1.093718632	1.475589216	-0.039864357
C	-2.074967737	0.407598312	-0.013161693
C	-3.456201509	0.659916103	-0.030982151
C	-4.350528401	-0.391435254	-0.004680099
C	-3.834730366	-1.724807817	0.040555239
C	-2.500240894	-1.905407498	0.055930207
C	-1.594365272	2.844913194	-0.085720676
C	2.053839548	0.130307270	0.022760977
C	2.802524315	-1.108720695	0.067768832
C	4.180835957	-1.089958780	0.076510201
C	4.890931093	0.119232222	0.042285609
C	4.161505677	1.337080468	-0.002059918
C	2.810946822	1.363950680	-0.011980178
H	4.701117941	2.266610923	-0.028471369
H	-3.806893245	1.672678038	-0.065214650
H	-5.407636379	-0.209593466	-0.017771104
H	-4.490595992	-2.573135827	0.062128747
H	-2.056372506	-2.879789658	0.089492642
H	2.279712873	-2.038930905	0.094076279
H	4.713480843	-2.022424694	0.110102010
H	5.963933547	0.128626515	0.049241353
H	2.283317435	2.291079090	-0.045446699

### SA2-CASSCF(12,12) optimized MECI of compound 1

F	-0.704905050	-1.706934722	-2.179734886
F	0.315795979	-2.641764877	-0.401560762
B	-0.213182558	-1.516785265	-0.944699575
N	0.775145150	-0.254173236	-0.938097589
N	0.154089355	0.787149845	-1.593363375
N	-1.305764608	-0.910990785	0.056679704
N	-1.518438731	3.745626279	-1.034771700
C	-0.751009968	1.279189658	-0.739456020
C	-1.509199092	0.419930560	0.113299953
C	-2.544836228	0.916534472	0.967753196
C	-3.326190271	0.043028241	1.661894229
C	-3.105862252	-1.362320484	1.542520332
C	-2.106378962	-1.775764831	0.744897299
C	-1.177755523	2.641371132	-0.922586287
C	1.757717064	0.036573451	-0.041491197
C	2.215196171	-0.924839790	0.894285147
C	3.248951611	-0.599596337	1.764990116
C	3.847904817	0.657074576	1.721926494
C	3.415728459	1.596926553	0.773102542
C	2.408067550	1.307993117	-0.093386309
H	3.901530741	2.553993352	0.715422580
H	-2.697610591	1.975438558	1.031840385
H	-4.108747018	0.413424548	2.297904852
H	-3.704170849	-2.070336535	2.081001047
H	-1.863811848	-2.810490709	0.613687400
H	1.768213250	-1.893379933	0.933243903
H	3.583738817	-1.331481595	2.476822073
H	4.649180904	0.900014200	2.394639078
H	2.109462339	2.014298460	-0.840372994

### B3LYP/TZVP optimized S<sub>0</sub>-min geometry of compound 2

F	-0.256601000	-2.117640000	-0.736457000
F	-0.609415000	-1.743391000	1.493648000
B	-0.683084000	-1.196503000	0.210673000
N	0.139120000	0.124548000	0.124347000
N	-0.392331000	1.322107000	0.183327000
N	-2.199742000	-0.839932000	-0.080346000
N	-2.509247000	3.925215000	0.360612000
C	-1.692433000	1.483530000	0.166495000
C	-2.671232000	0.430049000	-0.014582000
C	-4.038056000	0.673944000	-0.178145000
C	-4.897441000	-0.380608000	-0.412420000

C	-4.390100000	-1.678923000	-0.491280000
C	-3.040488000	-1.872091000	-0.319251000
C	-2.134804000	2.836811000	0.271638000
C	1.557785000	0.107905000	0.045254000
C	2.268876000	-1.024302000	0.459491000
C	3.650500000	-1.044571000	0.380354000
C	4.345048000	0.066365000	-0.113667000
C	3.631675000	1.198866000	-0.529657000
C	2.251410000	1.215920000	-0.456165000
C	5.769160000	0.045500000	-0.194533000
N	6.922170000	0.029260000	-0.260131000
H	4.160423000	2.057606000	-0.920754000
H	-4.405326000	1.688482000	-0.126075000
H	-5.956129000	-0.198416000	-0.538700000
H	-5.031946000	-2.527121000	-0.678180000
H	-2.584575000	-2.849739000	-0.362413000
H	1.751403000	-1.881927000	0.861499000
H	4.193434000	-1.920148000	0.709470000
H	1.703084000	2.084319000	-0.788774000

### B3LYP/TZVP optimized S<sub>1</sub>-min geometry of compound 2

F	-0.383324000	-1.940947000	-1.146332000
F	-0.382701000	-1.942546000	1.145133000
B	-0.677057000	-1.201869000	0.000018000
N	0.174803000	0.131165000	0.000599000
N	-0.367050000	1.403111000	0.001102000
N	-2.196974000	-0.855377000	0.000638000
N	-2.526954000	3.936758000	-0.000059000
C	-1.689341000	1.490993000	0.000116000
C	-2.661690000	0.442350000	-0.000425000
C	-4.049793000	0.674269000	-0.001307000
C	-4.932636000	-0.380445000	-0.000899000
C	-4.430976000	-1.699597000	0.000465000
C	-3.073753000	-1.890593000	0.001127000
C	-2.156858000	2.842525000	0.000027000
C	1.526871000	0.109269000	0.000513000
C	2.242615000	-1.134459000	-0.000027000
C	3.609790000	-1.148317000	-0.000386000
C	4.343515000	0.062450000	-0.000127000
C	3.655870000	1.294842000	0.000560000
C	2.287081000	1.328449000	0.000920000
C	5.760136000	0.036106000	-0.000525000

N	6.917270000	0.013527000	-0.000852000
H	4.216501000	2.219707000	0.000848000
H	-4.411641000	1.692823000	-0.002276000
H	-5.998384000	-0.198286000	-0.001579000
H	-5.090252000	-2.555052000	0.000957000
H	-2.633734000	-2.877400000	0.002049000
H	1.705645000	-2.068312000	-0.000176000
H	4.136920000	-2.092400000	-0.000822000
H	1.761803000	2.268353000	0.001497000

**SA2-CASSCF(12,12) optimized S<sub>0</sub>-min geometry of compound 2**

F	-0.336467465	-2.066004644	-0.848057589
F	-0.536448954	-1.791932276	1.383118464
B	-0.667900966	-1.207808394	0.157655615
N	0.141506048	0.116084651	0.069585699
N	-0.393235743	1.290612301	0.083137166
N	-2.205461850	-0.827782970	-0.030939603
N	-2.567143280	3.917589087	0.130443137
C	-1.685192091	1.474548783	0.081457103
C	-2.660013653	0.419381007	-0.011348380
C	-4.039897450	0.659066992	-0.110933430
C	-4.890874613	-0.404606465	-0.232205463
C	-4.390463658	-1.708445557	-0.261136018
C	-3.043876687	-1.873664001	-0.158642032
C	-2.134479810	2.840989670	0.109296991
C	1.554790462	0.110502673	0.027183701
C	2.257914253	-1.083187782	0.258163148
C	3.641205119	-1.088652916	0.212648144
C	4.345550822	0.092702510	-0.060647774
C	3.649090852	1.266926489	-0.284328720
C	2.267741155	1.288203810	-0.243803132
C	5.787703212	0.080508314	-0.106781230
N	6.934208162	0.067221803	-0.143242018
H	4.184567132	2.174028955	-0.494580268
H	-4.401739856	1.667135681	-0.094550843
H	-5.949133939	-0.233660537	-0.308895155
H	-5.035868735	-2.558916606	-0.358023091
H	-2.577666848	-2.837137289	-0.171914418
H	1.739589981	-1.992299714	0.479129668
H	4.177237429	-2.001197288	0.392915177
H	1.742283995	2.203355639	-0.418168468

**SA2-CASSCF(12,12) optimized MECI of compound 2**

F	-0.392980080	-2.599391087	0.918600524
F	-1.603745450	-1.426933697	2.411571401
B	-0.968238307	-1.411310965	1.233855588
N	0.076044421	-0.163150207	1.215959748
N	-0.602047587	0.972857014	1.619056647
N	-1.871199110	-0.923886308	0.024611276
N	-1.858001893	3.872462336	0.229120532
C	-1.305666298	1.352421229	0.523796047
C	-1.982758082	0.396989310	-0.285421789
C	-2.823083200	0.761269928	-1.369630689
C	-3.527799296	-0.192034700	-2.031067371
C	-3.422674098	-1.552124404	-1.660596986
C	-2.587469080	-1.858711931	-0.642290201
C	-1.618605500	2.745595914	0.378317912
C	1.245998611	-0.032707131	0.558894645
C	1.863911180	-1.147442482	-0.080910803
C	3.081245135	-0.984232784	-0.713966935
C	3.716086360	0.268380700	-0.719555230
C	3.129174125	1.357919358	-0.063330531
C	1.930855949	1.225057803	0.571492701
C	4.985220506	0.425397064	-1.382660709
N	5.994551764	0.550506839	-1.912630693
H	3.640242254	2.302040322	-0.047159069
H	-2.902559604	1.796126614	-1.636842413
H	-4.170563428	0.092167978	-2.844282469
H	-3.966477837	-2.320901298	-2.172216529
H	-2.433281929	-2.866886162	-0.314920123
H	1.386849232	-2.102021956	-0.075817787
H	3.545203445	-1.817924549	-1.205306736
H	1.500671677	2.044530917	1.107328492

### B3LYP/TZVP optimized S<sub>0</sub>-min geometry of compound 3

F	-0.643141000	-2.093458000	-0.809432000
F	-0.966643000	-1.790127000	1.435652000
B	-1.054664000	-1.202796000	0.172796000
N	-0.228150000	0.118985000	0.117529000
N	-0.758360000	1.319154000	0.187381000
N	-2.574814000	-0.835439000	-0.088596000
N	-2.863961000	3.928106000	0.381595000
C	-2.055706000	1.484402000	0.170078000
C	-3.041052000	0.435199000	-0.010346000
C	-4.407940000	0.685773000	-0.155367000
C	-5.274902000	-0.364779000	-0.383049000

C	-4.773740000	-1.664100000	-0.473322000
C	-3.422204000	-1.863208000	-0.320143000
C	-2.493582000	2.839198000	0.285249000
C	1.187549000	0.101522000	0.054206000
C	1.889611000	-1.061213000	0.401197000
C	3.271271000	-1.083995000	0.339976000
C	3.953869000	0.056621000	-0.068579000
C	3.274614000	1.219906000	-0.419419000
C	1.894291000	1.238436000	-0.363613000
N	5.414792000	0.033628000	-0.129862000
O	5.994539000	-1.011271000	0.160407000
O	6.000312000	1.060607000	-0.468608000
H	3.823496000	2.091552000	-0.743320000
H	-4.770640000	1.701370000	-0.093410000
H	-6.334371000	-0.177867000	-0.494812000
H	-5.421052000	-2.509227000	-0.655207000
H	-2.971008000	-2.842551000	-0.373798000
H	1.364643000	-1.941336000	0.738323000
H	3.817283000	-1.973906000	0.614962000
H	1.355189000	2.129919000	-0.644618000

### B3LYP/TZVP optimized S<sub>1</sub>-min geometry of compound 3

F	-0.753176000	-1.930028000	-1.146643000
F	-0.752877000	-1.929794000	1.146567000
B	-1.048596000	-1.202865000	-0.000063000
N	-0.196401000	0.144018000	-0.000218000
N	-0.738037000	1.386233000	-0.000195000
N	-2.570491000	-0.851638000	0.000016000
N	-2.884043000	3.937484000	0.000046000
C	-2.064210000	1.488103000	0.000003000
C	-3.036501000	0.441270000	0.000121000
C	-4.423429000	0.674638000	0.000176000
C	-5.304789000	-0.383288000	0.000170000
C	-4.802726000	-1.697288000	0.000086000
C	-3.442528000	-1.887747000	0.000007000
C	-2.520284000	2.841104000	0.000008000
C	1.165010000	0.113608000	-0.000188000
C	1.868443000	-1.132058000	-0.000422000
C	3.238396000	-1.154972000	-0.000307000
C	3.955611000	0.052744000	0.000007000
C	3.295357000	1.289915000	0.000193000
C	1.925689000	1.328023000	0.000114000
N	5.400161000	0.019514000	0.000125000

O	5.962953000	-1.086764000	0.001031000
O	6.016575000	1.096813000	-0.000679000
H	3.871832000	2.202639000	0.000447000
H	-4.785889000	1.692802000	0.000234000
H	-6.370805000	-0.202688000	0.000213000
H	-5.460310000	-2.554040000	0.000090000
H	-3.001957000	-2.874245000	-0.000085000
H	1.328311000	-2.063958000	-0.000770000
H	3.771776000	-2.093143000	-0.000486000
H	1.405720000	2.271377000	0.000307000

**SA2-CASSCF(12,12) optimized  $S_0$ -min geometry of compound 3** (Because the state-specific gradients for state-averaged CASSCF in Firefly is computed in a seminumeric way, a very small imaginary frequency (15.10I) is obtained in the frequency calculation on this geometry even if we have increased the overall precision of computations as proposed in the Firefly documentation. The small imaginary frequency was verified to be a combination of translational and rotational motion.)

F	-0.716811806	-2.051401394	-0.888703233
F	-0.901033000	-1.820092819	1.348511202
B	-1.037789144	-1.211693021	0.135803888
N	-0.224278929	0.110837828	0.068009744
N	-0.755753795	1.287034518	0.087833461
N	-2.576104539	-0.823410734	-0.035200476
N	-2.921031717	3.921776115	0.144893010
C	-2.046950715	1.476343940	0.084701166
C	-3.025957893	0.424758078	-0.009630159
C	-4.405277112	0.669717116	-0.101721681
C	-5.260650677	-0.390828495	-0.221333460
C	-4.765304733	-1.696077336	-0.255435338
C	-3.418666663	-1.866166403	-0.160418582
C	-2.491424106	2.844030243	0.118875251
C	1.188583118	0.102073900	0.034148759
C	1.887249569	-1.101015664	0.230054335
C	3.270953899	-1.114470223	0.194482695
C	3.961110746	0.076102372	-0.035249533
C	3.291921077	1.261395750	-0.225648023
C	1.908257585	1.284158213	-0.192881183
N	5.412781651	0.058711598	-0.071935944
O	5.970664412	-0.997139056	0.097856464
O	5.989700972	1.098821418	-0.270437636
H	3.838893295	2.165608690	-0.401306441
H	-4.763399420	1.679006623	-0.080705989

H	-6.318666616	-0.215888612	-0.292350917
H	-5.414171688	-2.544072877	-0.350884948
H	-2.955928350	-2.831256514	-0.178185895
H	1.365583611	-2.015781811	0.416273781
H	3.807960835	-2.028011680	0.346560965
H	1.389477564	2.207539507	-0.340323372

### SA2-CASSCF(12,12) optimized MECI of compound 3

F	-0.784677094	-2.606984372	0.996935283
F	-2.047146551	-1.406441808	2.423400928
B	-1.361659195	-1.410643284	1.274292428
N	-0.301570656	-0.172921950	1.291351833
N	-0.981321925	0.974055342	1.652042310
N	-2.201645748	-0.924271354	0.021882786
N	-2.136513396	3.873869520	0.175578317
C	-1.631893494	1.350612969	0.521883447
C	-2.284741287	0.394968799	-0.305089575
C	-3.072869851	0.757336782	-1.429112929
C	-3.758258581	-0.194564292	-2.111661217
C	-3.684008695	-1.552657077	-1.724689267
C	-2.897997041	-1.858242242	-0.668233957
C	-1.919003229	2.745766308	0.347461000
C	0.901976320	-0.062223696	0.685643724
C	1.533127332	-1.189474885	0.084541320
C	2.781685423	-1.051847746	-0.491803285
C	3.414644511	0.193565039	-0.466662308
C	2.833771747	1.297768397	0.140114870
C	1.599463650	1.183268436	0.719374763
N	4.726321326	0.327946867	-1.074604126
O	5.211249998	-0.649349797	-1.588969058
O	5.258706429	1.409129870	-1.034835957
H	3.360411979	2.229909843	0.167354069
H	-3.128907091	1.790345517	-1.709007087
H	-4.362098517	0.088389200	-2.954601897
H	-4.212507870	-2.320499915	-2.253463453
H	-2.768733933	-2.864869905	-0.325713449
H	1.043228974	-2.137421852	0.072350048
H	3.262445523	-1.888380299	-0.955073657
H	1.157143626	2.014561098	1.226113702

### B3LYP/TZVP optimized S<sub>0</sub>-min geometry of compound 4

F	-0.421195000	-2.180652000	-0.598275000
F	-0.921077000	-1.716192000	1.587559000

B	-0.881758000	-1.211470000	0.282403000
N	-0.008766000	0.074615000	0.220485000
N	-0.493869000	1.281496000	0.307066000
N	-2.353890000	-0.804572000	-0.127798000
N	-2.544631000	3.941279000	0.527354000
C	-1.796616000	1.487549000	0.252646000
C	-2.788732000	0.479017000	-0.035297000
C	-4.134946000	0.773443000	-0.290394000
C	-5.002057000	-0.237749000	-0.643714000
C	-4.527864000	-1.549025000	-0.754104000
C	-3.204275000	-1.795134000	-0.488257000
C	-2.199987000	2.845658000	0.401538000
C	1.415204000	-0.003537000	0.138969000
C	2.097743000	-1.082134000	0.712752000
C	3.476470000	-1.154308000	0.631857000
C	4.204782000	-0.153707000	-0.021784000
C	3.525807000	0.922623000	-0.597341000
C	2.138908000	0.986182000	-0.521356000
O	5.555436000	-0.317453000	-0.046487000
C	6.354973000	0.674663000	-0.694654000
H	4.057769000	1.704701000	-1.119006000
H	-4.475028000	1.796234000	-0.216766000
H	-6.042084000	-0.014651000	-0.840875000
H	-5.178502000	-2.364295000	-1.034068000
H	-2.774129000	-2.783635000	-0.545067000
H	1.555518000	-1.854466000	1.239513000
H	4.009834000	-1.982035000	1.081093000
H	1.615963000	1.812425000	-0.982483000
H	7.383850000	0.341936000	-0.585746000
H	6.107989000	0.750291000	-1.756304000
H	6.236209000	1.651075000	-0.218885000

#### B3LYP/TZVP optimized S<sub>1</sub>-min geometry of compound 4

F	-0.637922000	-1.996441000	-1.143985000
F	-0.638208000	-1.996405000	1.144116000
B	-0.881904000	-1.220490000	0.000034000
N	0.021715000	0.048684000	0.000103000
N	-0.446209000	1.348092000	0.000024000
N	-2.387289000	-0.800778000	-0.000149000
N	-2.466336000	4.004460000	0.000253000
C	-1.753967000	1.518823000	0.000049000
C	-2.785011000	0.519879000	0.000007000
C	-4.157520000	0.822145000	0.000026000

C	-5.095331000	-0.184504000	-0.000133000
C	-4.661956000	-1.530474000	-0.000307000
C	-3.318220000	-1.789882000	-0.000297000
C	-2.149585000	2.893168000	0.000155000
C	1.394692000	-0.031664000	0.000117000
C	2.052638000	-1.296771000	0.000424000
C	3.418653000	-1.372060000	0.000411000
C	4.211257000	-0.199546000	0.000096000
C	3.580627000	1.057758000	-0.000198000
C	2.206478000	1.140851000	-0.000178000
O	5.534769000	-0.393820000	0.000138000
C	6.425877000	0.734766000	-0.000482000
H	4.162203000	1.968111000	-0.000426000
H	-4.465383000	1.858539000	0.000163000
H	-6.150307000	0.052780000	-0.000129000
H	-5.365225000	-2.350326000	-0.000440000
H	-2.927985000	-2.797428000	-0.000405000
H	1.474998000	-2.206713000	0.000673000
H	3.918078000	-2.331816000	0.000640000
H	1.724556000	2.104183000	-0.000398000
H	7.425882000	0.312708000	-0.000752000
H	6.277040000	1.340008000	-0.895643000
H	6.277711000	1.340440000	0.894502000

#### SA2-CASSCF(12,12) optimized S<sub>0</sub>-min geometry of compound 4

F	-0.463265559	-2.140096905	-0.648826846
F	-0.839194457	-1.697278451	1.537711672
B	-0.896972127	-1.224206767	0.260095453
N	-0.002600441	0.087761882	0.169907584
N	-0.476691209	1.258888779	0.202522500
N	-2.350007671	-0.794118785	-0.095259561
N	-2.581680040	3.950957957	0.336558811
C	-1.815161276	1.477190526	0.198486488
C	-2.759263828	0.465706038	-0.019483719
C	-4.160826070	0.751569240	-0.211619467
C	-5.016068175	-0.261682043	-0.490001736
C	-4.529377027	-1.603990266	-0.594244154
C	-3.224631195	-1.816555755	-0.394360008
C	-2.209330250	2.853049709	0.275156399
C	1.412414411	-0.001616257	0.098532641
C	2.069351802	-1.169574383	0.507380135
C	3.454361524	-1.232323542	0.440450061
C	4.209010248	-0.138181414	-0.028672098

C	3.558733780	1.005164300	-0.426258955
C	2.167950450	1.077715732	-0.366071670
O	5.541272329	-0.324490193	-0.044724395
C	6.377370187	0.709280464	-0.484401972
H	4.097972188	1.856127708	-0.793622279
H	-4.489635669	1.768465413	-0.138358089
H	-6.060029676	-0.056847359	-0.640068071
H	-5.187744726	-2.419171843	-0.821049171
H	-2.775123338	-2.785891307	-0.449119790
H	1.523164109	-2.009539630	0.882693259
H	3.976893031	-2.116246844	0.752942130
H	1.675148260	1.974463557	-0.682213843
H	7.386803928	0.336237336	-0.401819479
H	6.175317609	0.967327366	-1.518434227
H	6.270863374	1.593160257	0.135232383

**SA2-CASSCF(12,12) optimized S<sub>1</sub>-min geometry of compound 4** (Because the state-specific gradients for state-averaged CASSCF in Firefly is computed in a seminumeric way, a very small imaginary frequency (16.71I) is obtained in the frequency calculation on this geometry even if we have increased the overall precision of computations as proposed in the Firefly documentation. The small imaginary frequency was verified to be a combination of translational and rotational motion.)

F	-0.575987084	-2.193002911	-0.805165329
F	-0.668176562	-1.777183685	1.410264700
B	-0.872414414	-1.255884733	0.156499366
N	0.022711334	0.017600576	-0.038515936
N	-0.468474926	1.333748751	-0.004164142
N	-2.357869438	-0.838913371	-0.008697382
N	-2.518073609	3.971056788	0.034115043
C	-1.722771338	1.478282946	-0.012799132
C	-2.754367250	0.460358550	-0.047373180
C	-4.120975208	0.779713436	-0.127282265
C	-5.062390819	-0.227056805	-0.173202518
C	-4.613328726	-1.585180335	-0.139256331
C	-3.291194510	-1.829577946	-0.059392621
C	-2.153038855	2.871748693	0.015146132
C	1.356652508	-0.020374480	-0.017700515
C	2.056410975	-1.282381510	0.026261860
C	3.421029275	-1.317096487	0.039705718
C	4.192349719	-0.121865721	0.008673480
C	3.534444308	1.102633511	-0.033405160
C	2.163505706	1.167521283	-0.044226799

O	5.513639437	-0.292337477	0.024722103
C	6.370670091	0.820944168	0.001555833
H	4.087728471	2.021273984	-0.055309269
H	-4.420869651	1.808927341	-0.155564530
H	-6.107889552	0.005653218	-0.235096518
H	-5.308524154	-2.400965183	-0.177963858
H	-2.894614194	-2.824170500	-0.033740738
H	1.501674487	-2.194516126	0.043884158
H	3.944882644	-2.253377550	0.074739062
H	1.679756690	2.118286977	-0.071800915
H	7.373708399	0.425047588	0.022155153
H	6.230681894	1.401682134	-0.902701489
H	6.213845409	1.451403428	0.868976162

#### SA2-CASSCF(12,12) optimized MECI of compound 4

F	-1.807866383	-1.695201064	-2.197694453
F	-0.600303919	-2.738770716	-0.595998686
B	-1.102551994	-1.559671038	-1.056861241
N	-0.011577738	-0.440399063	-1.216163273
N	-0.648737744	0.783803762	-1.735400711
N	-2.000844504	-0.902978741	0.099787072
N	-1.847827354	3.818623287	-0.709729095
C	-1.356903205	1.264215561	-0.709302902
C	-2.068065461	0.431931647	0.214658198
C	-2.920791738	0.986328987	1.221111181
C	-3.680018166	0.160421760	1.995084583
C	-3.617206447	-1.251005103	1.806545613
C	-2.779042805	-1.719408190	0.864753296
C	-1.635578833	2.676987918	-0.724623240
C	1.136495138	-0.250829763	-0.522533372
C	1.616682706	-1.197894952	0.421098801
C	2.787686169	-0.977789287	1.083043201
C	3.547398472	0.178361135	0.842370068
C	3.110936932	1.102325071	-0.103166078
C	1.934858117	0.883023848	-0.783621843
O	4.671335573	0.288794133	1.549121521
C	5.506148407	1.408228292	1.387521378
H	3.688921604	1.975014976	-0.333743704
H	-2.962653803	2.050902546	1.335837331
H	-4.327981761	0.575987309	2.744594614
H	-4.201972407	-1.923062640	2.402958116
H	-2.654663220	-2.765207832	0.670944821
H	1.054604048	-2.085162775	0.618061895

H	3.154032371	-1.683384189	1.804341245
H	1.622158839	1.570202416	-1.542884937
H	6.327389113	1.266826474	2.072162850
H	5.887902896	1.467478193	0.375126205
H	4.983213912	2.324239521	1.635834171

**B3LYP/TZVP optimized S<sub>0</sub>-min geometry of compound 5**

F	-0.655988000	-2.128711000	-0.636852000
F	-1.163946000	-1.716232000	1.558140000
B	-1.154032000	-1.191827000	0.259298000
N	-0.335750000	0.132650000	0.216074000
N	-0.874489000	1.312619000	0.326950000
N	-2.641924000	-0.845154000	-0.140655000
N	-3.043190000	3.873724000	0.599713000
C	-2.189978000	1.460835000	0.280060000
C	-3.134354000	0.416528000	-0.021519000
C	-4.496568000	0.651750000	-0.263288000
C	-5.317316000	-0.390466000	-0.631618000
C	-4.783130000	-1.677304000	-0.771919000
C	-3.449018000	-1.866786000	-0.518070000
C	-2.651794000	2.795913000	0.453621000
C	1.086907000	0.115717000	0.123426000
C	1.824515000	-0.951663000	0.640763000
C	3.205866000	-0.967328000	0.555254000
C	3.920037000	0.094306000	-0.047250000
C	3.153717000	1.156187000	-0.583648000
C	1.773464000	1.161165000	-0.498163000
C	5.985624000	1.116417000	-0.879941000
C	6.037827000	-1.091434000	0.287033000
N	5.293392000	0.096206000	-0.106030000
H	3.637972000	1.979580000	-1.086846000
H	-4.882921000	1.656117000	-0.167332000
H	-6.367931000	-0.212425000	-0.818336000
H	-5.397365000	-2.515853000	-1.065066000
H	-2.974222000	-2.833092000	-0.596719000
H	1.322951000	-1.774939000	1.130018000
H	3.732418000	-1.812739000	0.971754000
H	1.216474000	1.982409000	-0.928267000
H	5.752632000	1.060018000	-1.950486000
H	5.731559000	2.118245000	-0.527213000
H	7.057514000	0.985280000	-0.756787000
H	5.824336000	-1.366146000	1.322304000
H	5.813479000	-1.955517000	-0.350461000

H	7.101581000	-0.880640000	0.214549000
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**B3LYP/TZVP optimized S<sub>1</sub>-min geometry of compound 5**

F	-0.847065000	-1.996344000	-1.085779000
F	-0.907167000	-1.934486000	1.199459000
B	-1.151759000	-1.192468000	0.027725000
N	-0.316379000	0.110511000	0.012965000
N	-0.840031000	1.374639000	0.030485000
N	-2.676665000	-0.844292000	-0.021935000
N	-2.969710000	3.952193000	0.076011000
C	-2.151384000	1.500427000	0.025699000
C	-3.137513000	0.455493000	-0.006466000
C	-4.521518000	0.692250000	-0.029436000
C	-5.411264000	-0.357006000	-0.066899000
C	-4.913843000	-1.681548000	-0.082585000
C	-3.560471000	-1.876689000	-0.058925000
C	-2.603670000	2.855944000	0.053506000
C	1.080493000	0.097425000	0.010567000
C	1.794861000	-1.121474000	0.061702000
C	3.169757000	-1.143498000	0.051049000
C	3.930992000	0.054972000	-0.009923000
C	3.209085000	1.274886000	-0.056022000
C	1.832663000	1.294703000	-0.045379000
C	6.058019000	1.268905000	-0.096703000
C	6.016560000	-1.236804000	0.041323000
N	5.294871000	0.029041000	-0.021843000
H	3.734696000	2.216945000	-0.099686000
H	-4.877283000	1.713244000	-0.018027000
H	-6.476139000	-0.169674000	-0.084616000
H	-5.577083000	-2.533674000	-0.112890000
H	-3.122170000	-2.864167000	-0.069520000
H	1.263883000	-2.058773000	0.110917000
H	3.665890000	-2.101328000	0.091080000
H	1.311630000	2.237433000	-0.081559000
H	5.814796000	1.825650000	-1.005434000
H	5.856384000	1.908774000	0.766708000
H	7.116879000	1.032757000	-0.110546000
H	5.777800000	-1.781132000	0.958576000
H	5.773712000	-1.872638000	-0.814125000
H	7.082681000	-1.036180000	0.028547000

**SA2-CASSCF(12,12) optimized S<sub>0</sub>-min geometry of compound 5 (Because the state-specific gradients for state-averaged CASSCF in Firefly is computed**

in a seminumeric way, a very small imaginary frequency (14.62I) is obtained in the frequency calculation on this geometry even if we have increased the overall precision of computations as proposed in the Firefly documentation. The small imaginary frequency was verified to be a combination of translational and rotational motion.)

F	-0.463265559	-2.140096905	-0.648826846
F	-0.839194457	-1.697278451	1.537711672
B	-0.896972127	-1.224206767	0.260095453
N	-0.002600441	0.087761882	0.169907584
N	-0.476691209	1.258888779	0.202522500
N	-2.350007671	-0.794118785	-0.095259561
N	-2.581680040	3.950957957	0.336558811
C	-1.815161276	1.477190526	0.198486488
C	-2.759263828	0.465706038	-0.019483719
C	-4.160826070	0.751569240	-0.211619467
C	-5.016068175	-0.261682043	-0.490001736
C	-4.529377027	-1.603990266	-0.594244154
C	-3.224631195	-1.816555755	-0.394360008
C	-2.209330250	2.853049709	0.275156399
C	1.412414411	-0.001616257	0.098532641
C	2.069351802	-1.169574383	0.507380135
C	3.454361524	-1.232323542	0.440450061
C	4.209010248	-0.138181414	-0.028672098
C	3.558733780	1.005164300	-0.426258955
C	2.167950450	1.077715732	-0.366071670
O	5.541272329	-0.324490193	-0.044724395
C	6.377370187	0.709280464	-0.484401972
H	4.097972188	1.856127708	-0.793622279
H	-4.489635669	1.768465413	-0.138358089
H	-6.060029676	-0.056847359	-0.640068071
H	-5.187744726	-2.419171843	-0.821049171
H	-2.775123338	-2.785891307	-0.449119790
H	1.523164109	-2.009539630	0.882693259
H	3.976893031	-2.116246844	0.752942130
H	1.675148260	1.974463557	-0.682213843
H	7.386803928	0.336237336	-0.401819479
H	6.175317609	0.967327366	-1.518434227
H	6.270863374	1.593160257	0.135232383

#### SA2-CASSCF(12,12) optimized S<sub>1</sub>-min geometry of compound 5

F	-0.802562244	-2.192254291	-0.757786639
F	-0.916854413	-1.691003499	1.438665325
B	-1.139554846	-1.224582856	0.163527033

N	-0.309948546	0.076067839	-0.082705479
N	-0.856482938	1.357491780	-0.010760303
N	-2.643470737	-0.883911429	-0.021441702
N	-3.009907195	3.913906692	0.112281448
C	-2.114556884	1.457689750	0.001053819
C	-3.102536013	0.396170017	-0.045045893
C	-4.480943760	0.652503927	-0.124880122
C	-5.375485491	-0.396569876	-0.188415918
C	-4.861658301	-1.732690209	-0.172490401
C	-3.529862328	-1.915753455	-0.090423107
C	-2.599570965	2.831413369	0.064821638
C	1.034406171	0.100483834	-0.054280953
C	1.795173786	-1.115589603	-0.022962537
C	3.151472006	-1.103491676	-0.004321281
C	3.905568348	0.100433088	-0.018230924
C	3.160136541	1.311124356	-0.050407147
C	1.785499102	1.319727663	-0.065647473
C	6.003278822	1.342498209	0.003541862
C	5.994096953	-1.158425869	0.048410511
N	5.266067691	0.094399422	-0.001775656
H	3.666539394	2.255204598	-0.060207011
H	-4.827507473	1.667434437	-0.140583481
H	-6.430647142	-0.212551612	-0.250735114
H	-5.517178164	-2.580048741	-0.226190979
H	-3.087235566	-2.890896553	-0.077659235
H	1.283116529	-2.052888159	-0.018370962
H	3.656505659	-2.048199286	0.022575614
H	1.265091683	2.251674859	-0.085556766
H	5.791604998	1.933046888	-0.881990457
H	5.772151374	1.939911532	0.880045717
H	7.060812665	1.129365643	0.015082968
H	5.760875891	-1.721211916	0.946901147
H	5.776297593	-1.779593151	-0.814252001
H	7.053095898	-0.952311031	0.049806916

### SA2-CASSCF(12,12) optimized MECI of compound 5

F	-2.185280884	-0.631736749	-3.032950784
F	-0.857353833	-2.169999447	-2.053764695
B	-1.399964719	-0.926991848	-1.980218095
N	-0.366371550	0.230848412	-1.702936350
N	-1.038734785	1.445529168	-1.725988633
N	-2.229234585	-0.809864521	-0.594275673
N	-2.428459411	3.892728086	0.248707736

C	-1.726631749	1.533706591	-0.595287579
C	-2.338695506	0.384466043	0.011606294
C	-3.145584554	0.486073093	1.185309430
C	-3.822231677	-0.609280656	1.636309517
C	-3.717468350	-1.846503994	0.939286131
C	-2.925430556	-1.889782195	-0.149463689
C	-2.118552149	2.846297075	-0.147268098
C	0.764031830	0.150723854	-0.950889960
C	1.316267862	-1.079253301	-0.524377112
C	2.477081118	-1.118528896	0.207414443
C	3.176229279	0.040697890	0.574527833
C	2.648653714	1.274523090	0.110387125
C	1.490672486	1.329989950	-0.628727973
C	5.126327313	1.184317138	1.497360771
C	4.956167957	-1.286561889	1.579049206
N	4.319505338	-0.008282170	1.339524448
H	3.164210429	2.193012509	0.304091282
H	-3.219694422	1.431912237	1.683998652
H	-4.435605482	-0.535630281	2.515277620
H	-4.235397185	-2.723594198	1.273843072
H	-2.777761523	-2.783772427	-0.720423392
H	0.832693949	-1.998501511	-0.772636185
H	2.842439137	-2.082451316	0.499516269
H	1.145000821	2.273966950	-0.998425742
H	5.530271114	1.546838364	0.553652357
H	4.554052308	1.981797126	1.954987092
H	5.953312033	0.964207250	2.155884098
H	4.292008958	-1.956938684	2.111287562
H	5.272832655	-1.774540936	0.658983575
H	5.827096695	-1.136180874	2.199388191