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Theoretical study of the excitation of proflavine H-dimer in an aqueous solution: the effect of functionals and dispersion corrections

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SUPPLEMENTARY MATERIAL

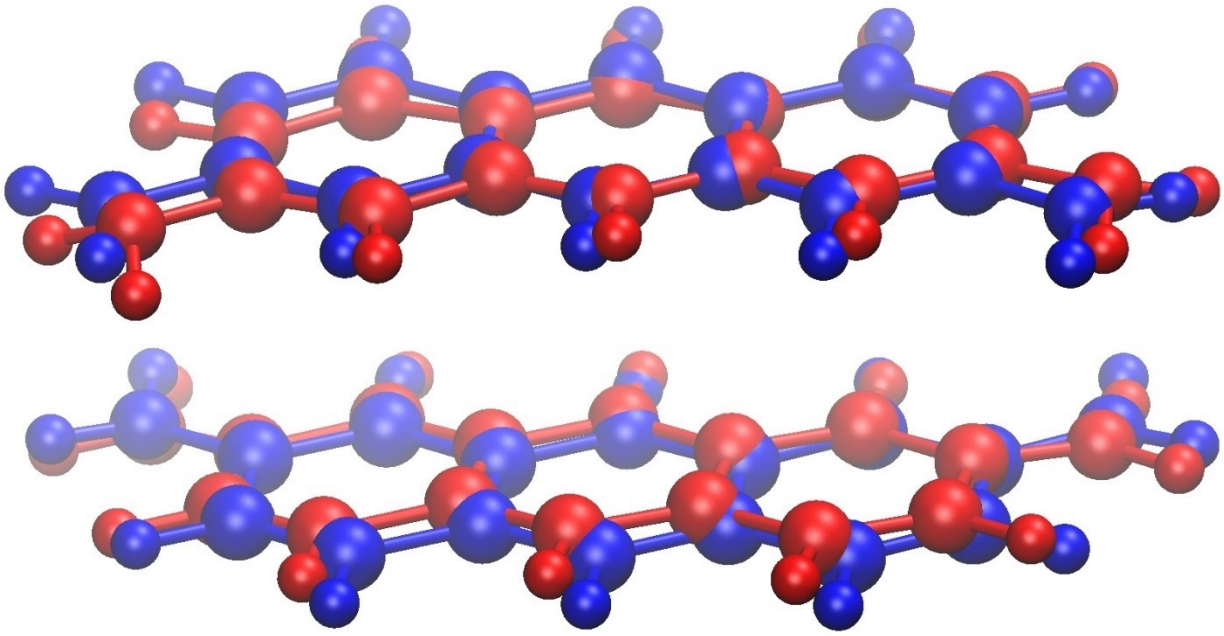

Fig. S1. Fitted structures of the proflavine dimer in the ground (blue) and excited (red) states, calculated using the APFD functional

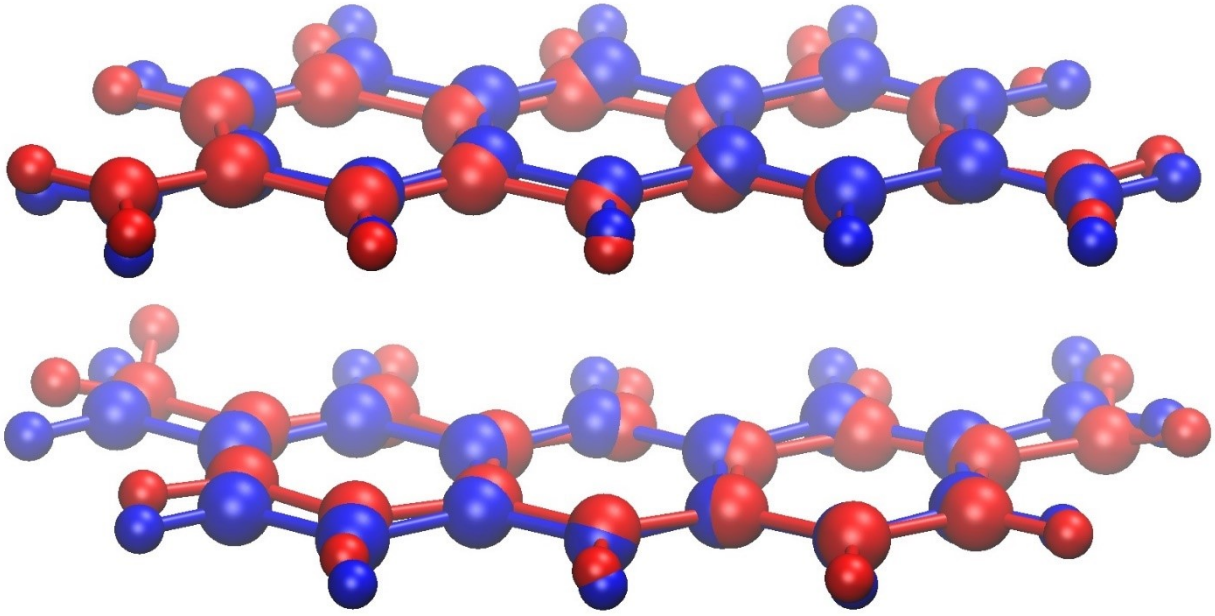

Fig. S2. Fitted structures of the proflavine dimer in the ground (blue) and excited (red) states, calculated using the B3LYP functional with GD2 correction

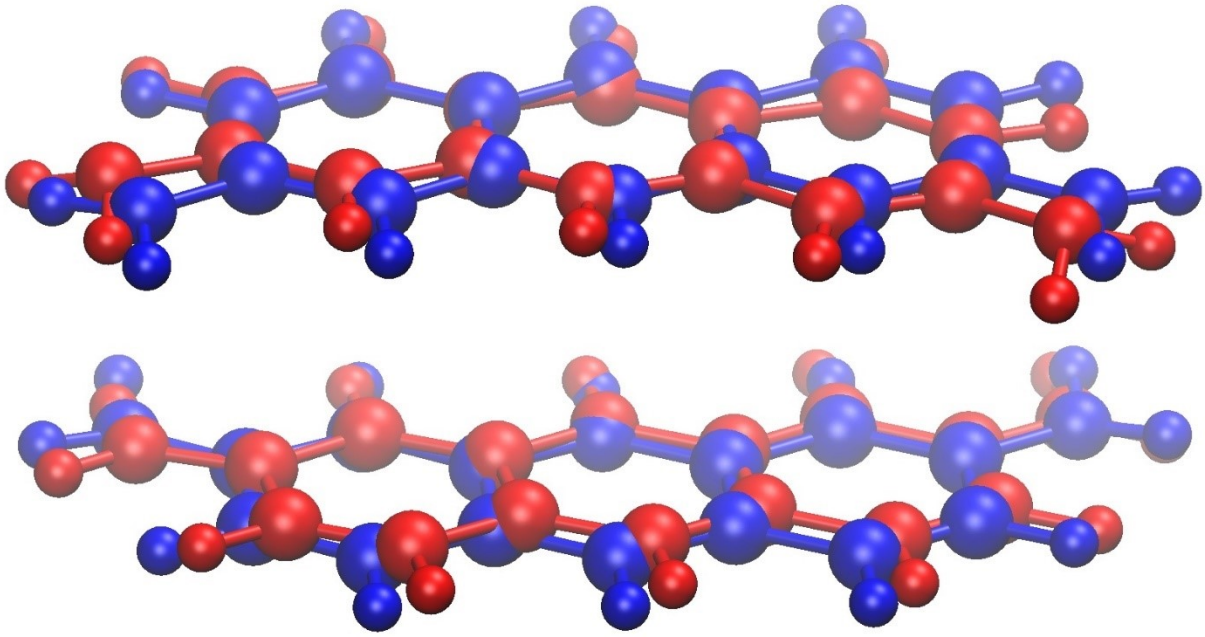

Fig. S3. Fitted structures of the proflavine dimer in the ground (blue) and excited (red) states, calculated using the B3LYP functional with GD3 correction

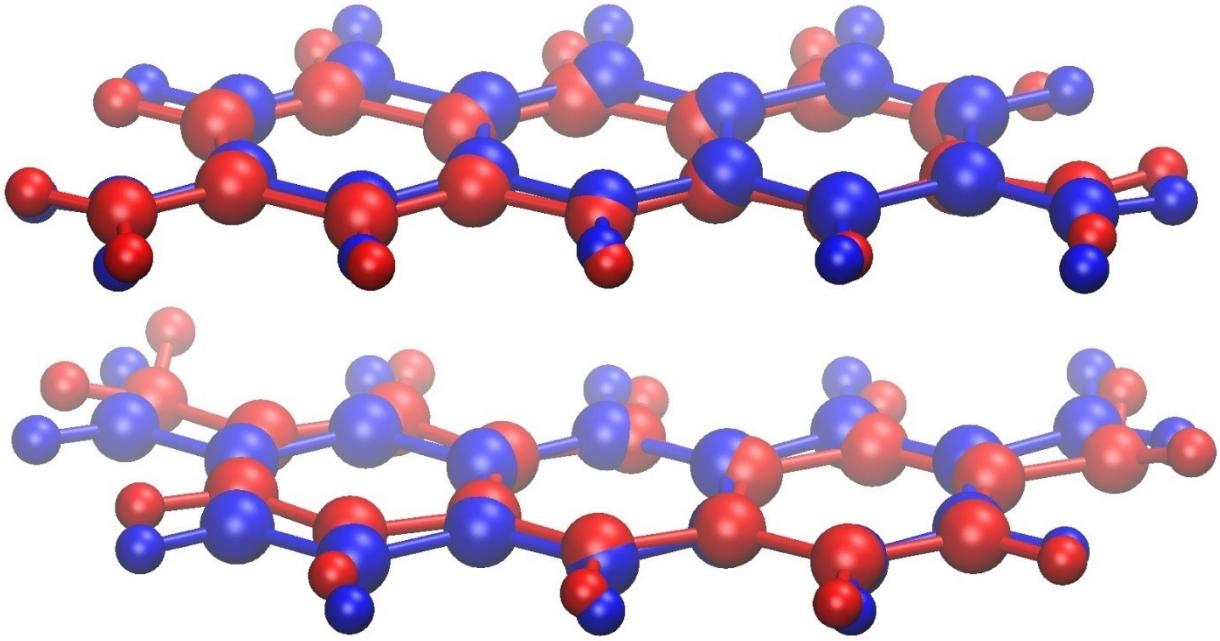

Fig. S4. Fitted structures of the proflavine dimer in the ground (blue) and excited (red) states, calculated using the B3LYP functional with GD3+BJ correction

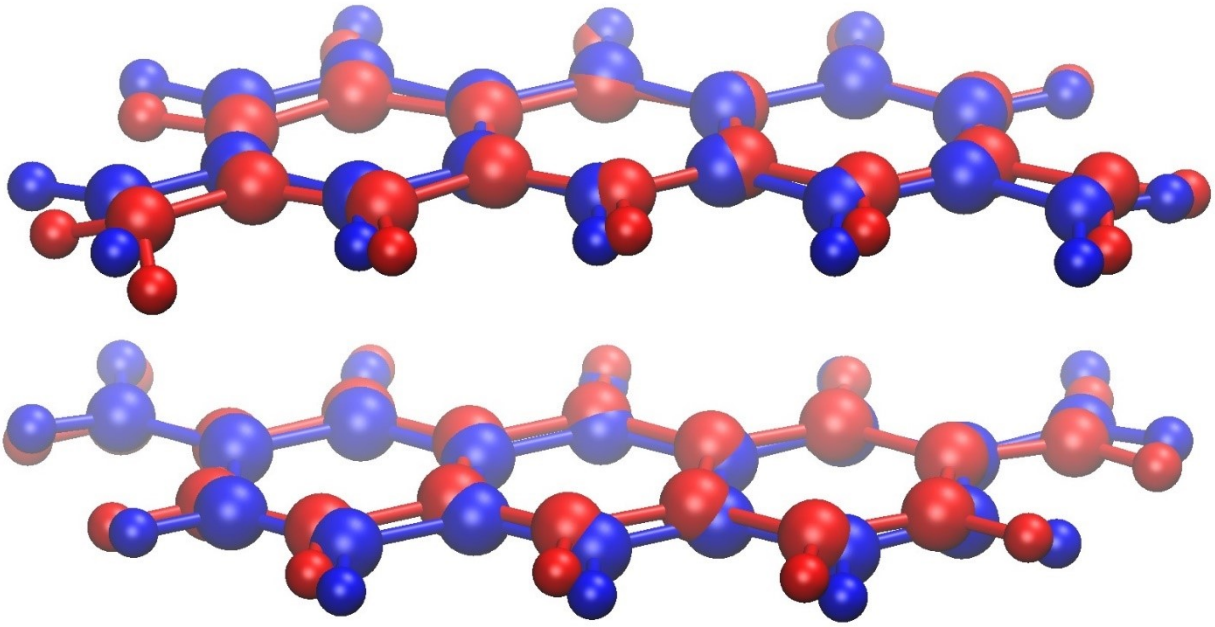

Fig. S5. Fitted structures of the proflavine dimer in the ground (blue) and excited (red) states, calculated using the B3PW91 functional with GD3 correction

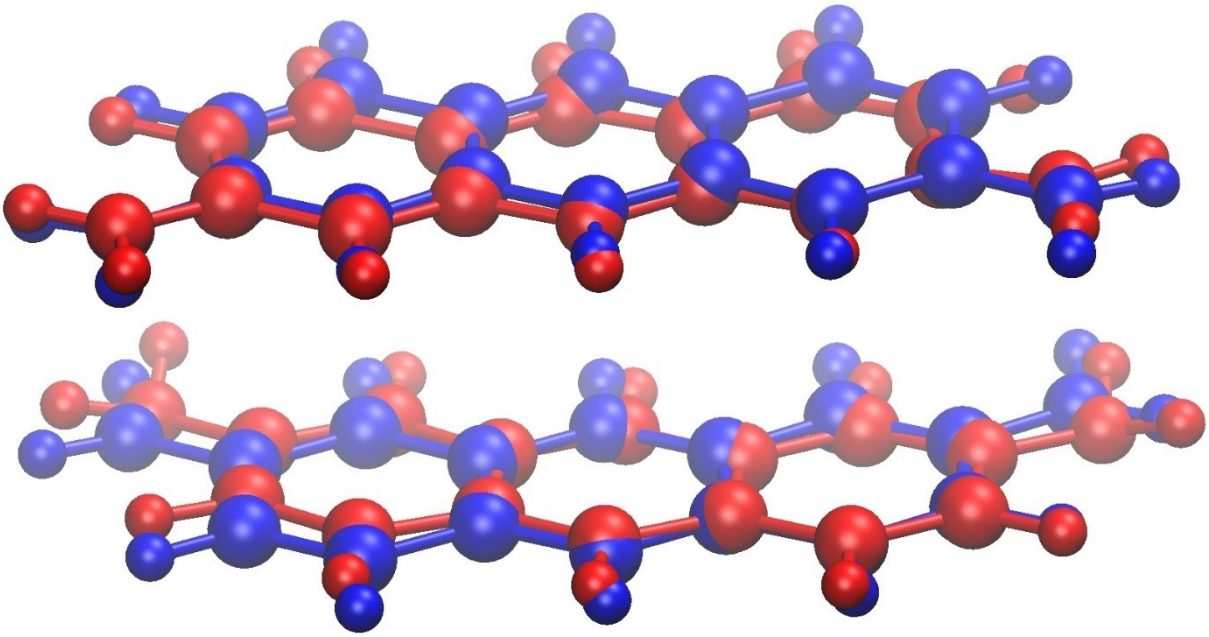

Fig. S6. Fitted structures of the proflavine dimer in the ground (blue) and excited (red) states, calculated using the B3PW91 functional with GD3+BJ correction

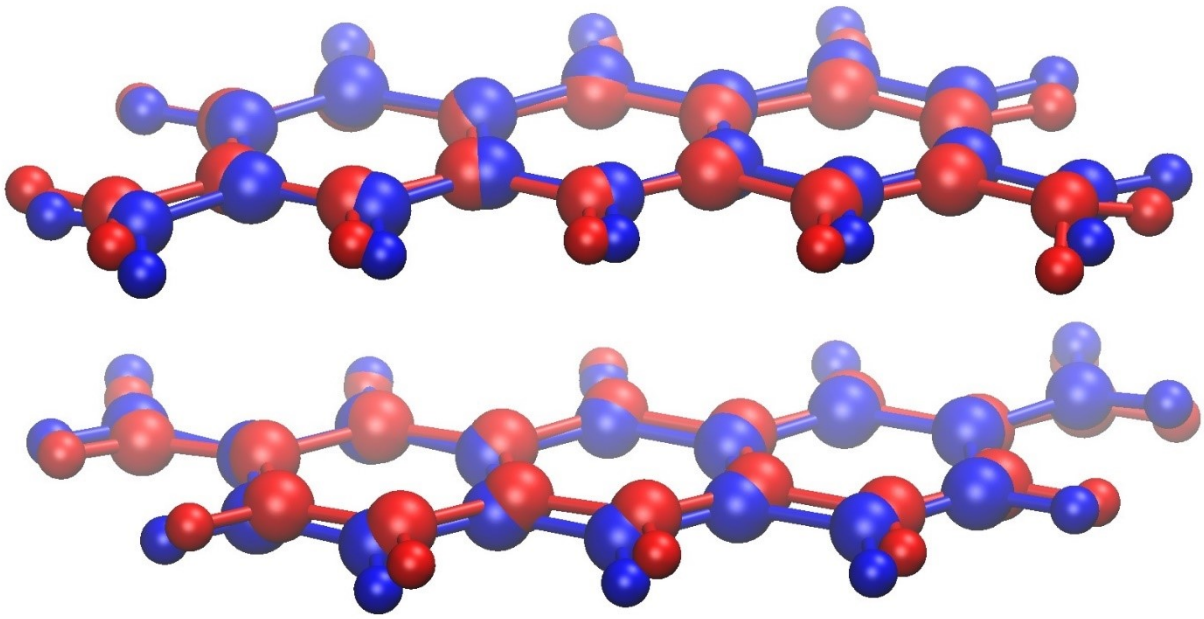

Fig. S7. Fitted structures of the proflavine dimer in the ground (blue) and excited (red) states, calculated using the BMK functional with GD3 correction

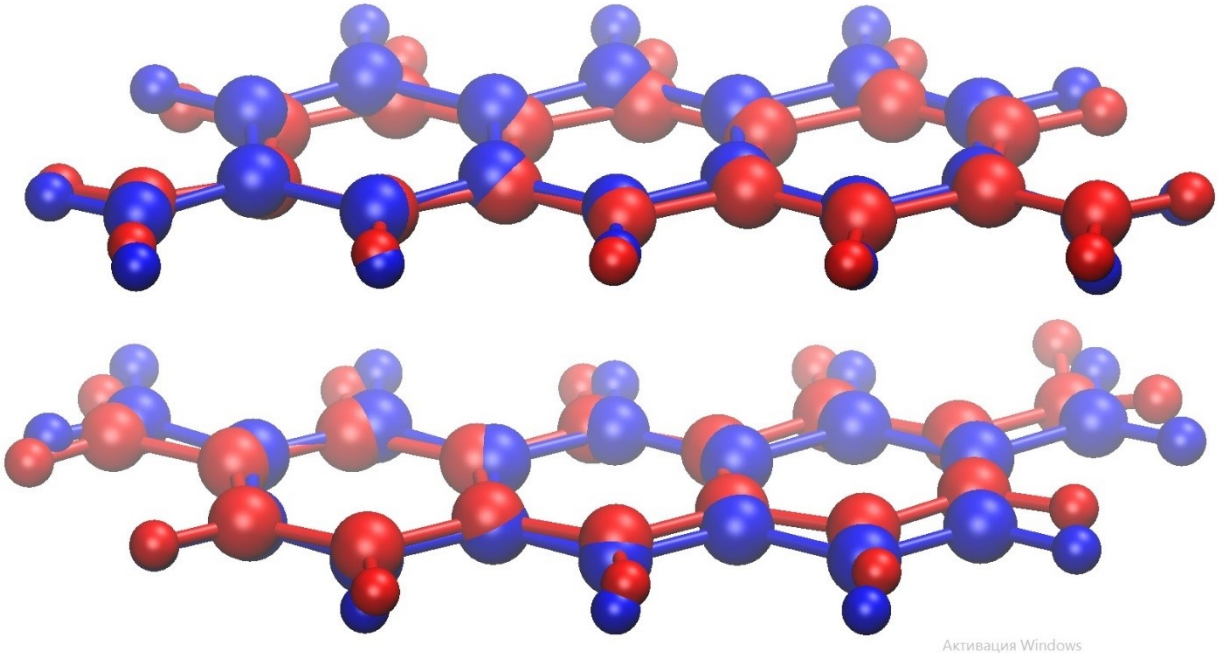

Fig. S8. Fitted structures of the proflavine dimer in the ground (blue) and excited (red) states, calculated using the BMK functional with GD3+BJ correction

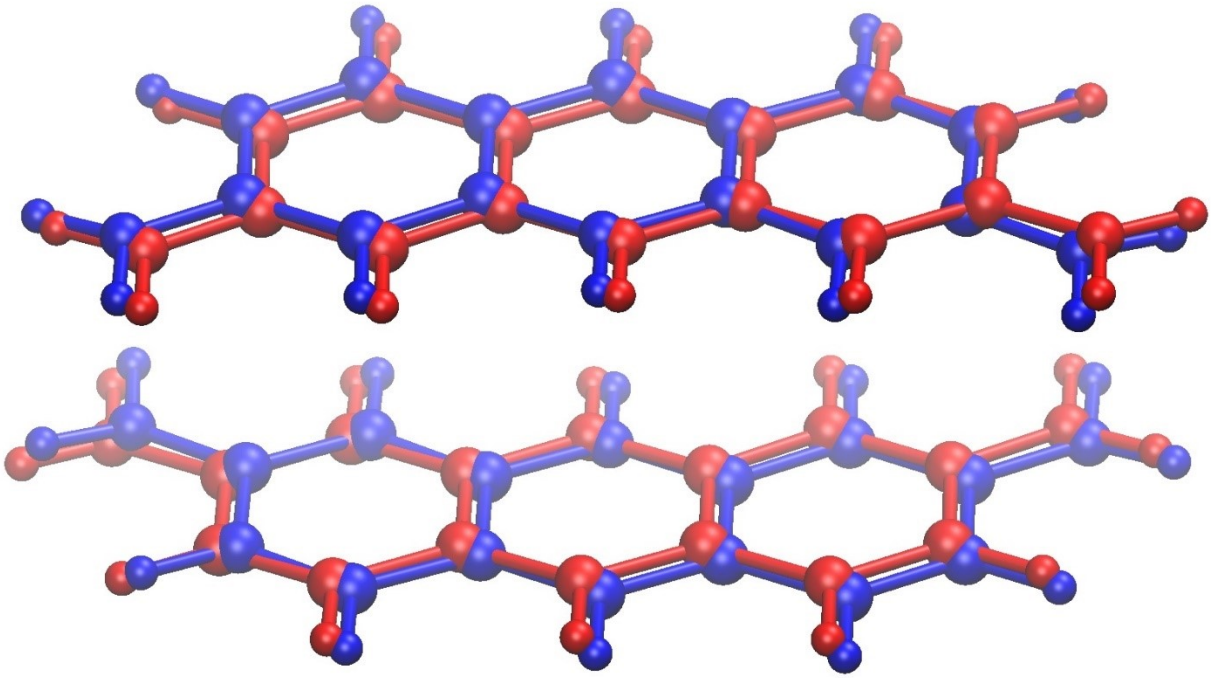

Fig. S9. Fitted structures of the proflavine dimer in the ground (blue) and excited (red) states, calculated using the CAM-B3LYP functional with GD3 correction

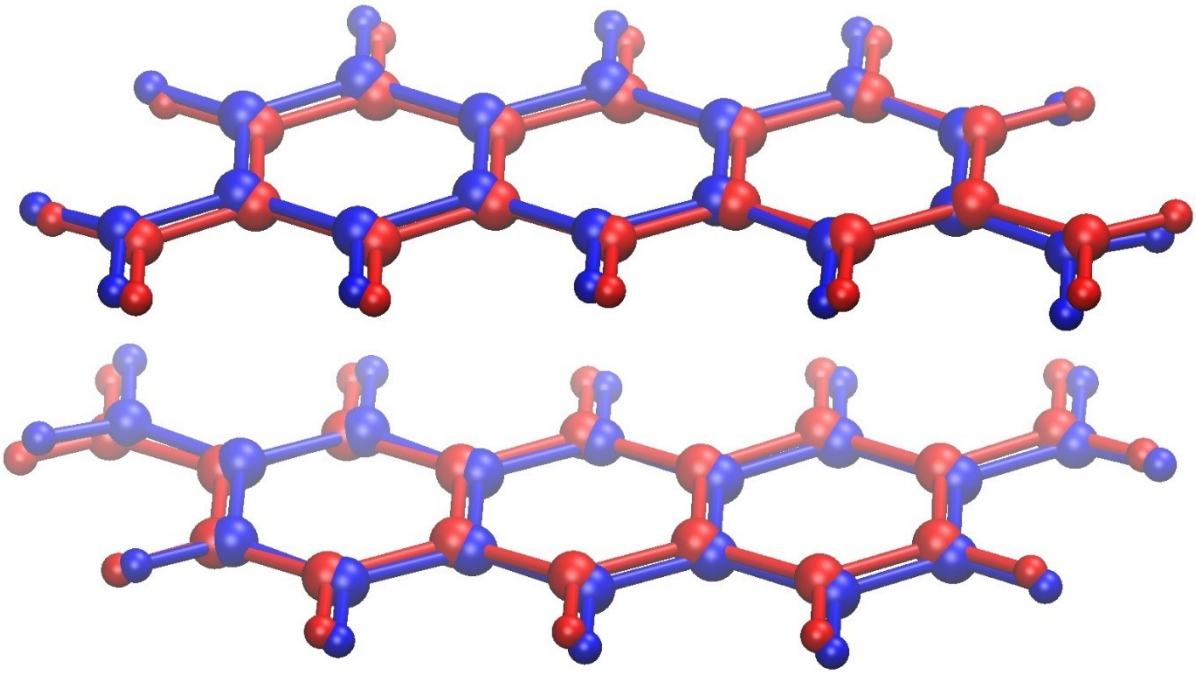

Fig. S10. Fitted structures of the proflavine dimer in the ground (blue) and excited (red) states, calculated using the CAM-B3LYP functional with GD3+BJ correction

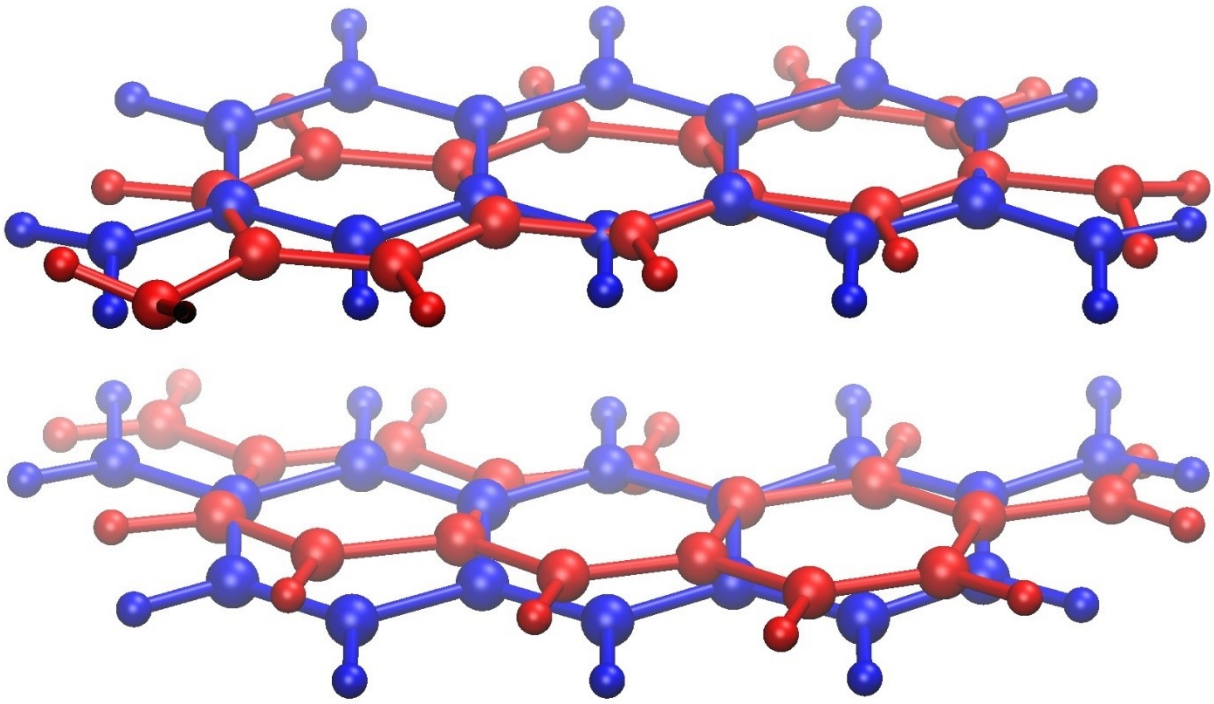

Fig. S11. Fitted structures of the proflavine dimer in the ground (blue) and excited (red) states, calculated using the M05 functional with GD3 correction

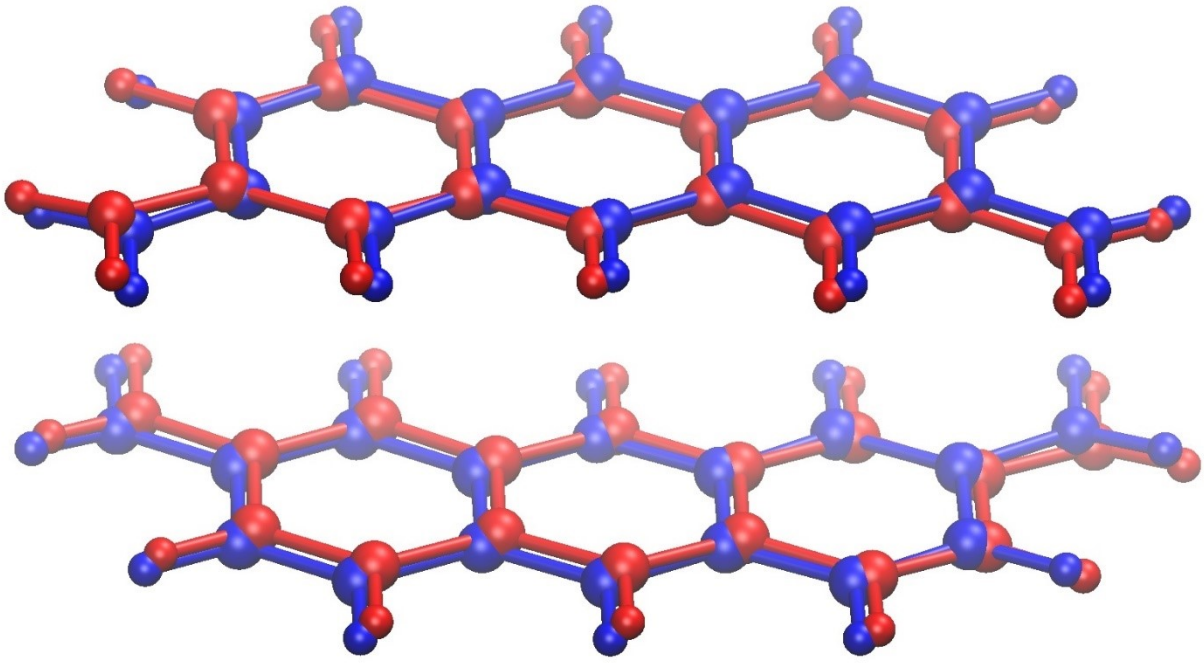

Fig. S12. Fitted structures of the proflavine dimer in the ground (blue) and excited (red) states, calculated using the M052X functional

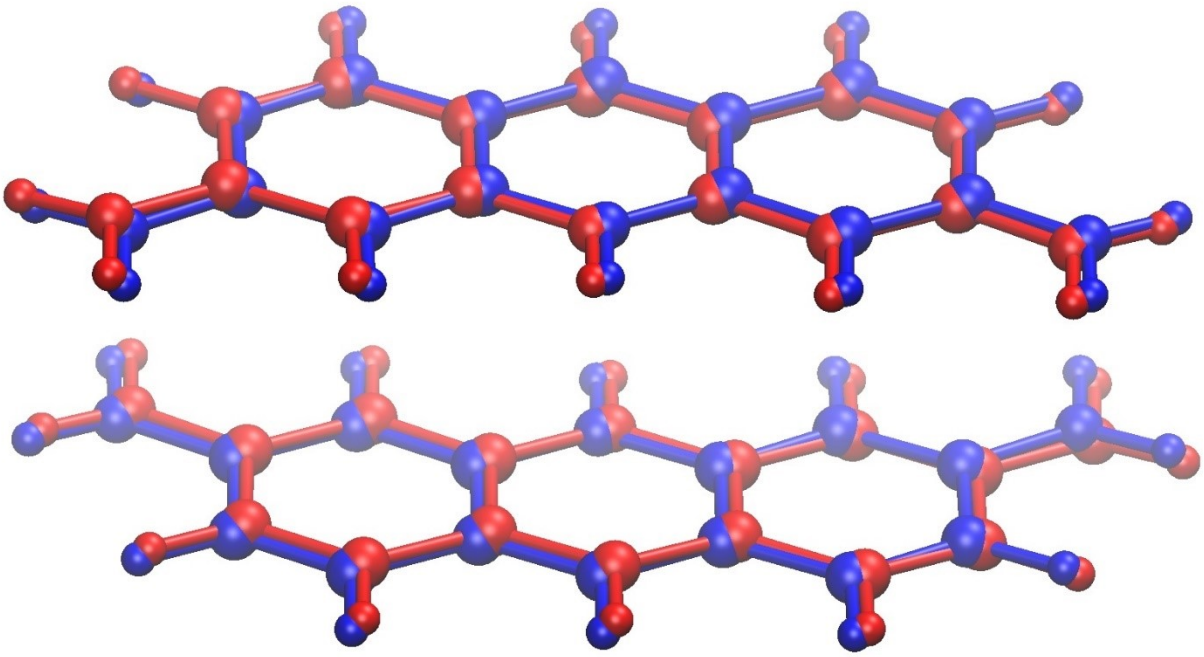

Fig. S13. Fitted structures of the proflavine dimer in the ground (blue) and excited (red) states, calculated using the M062X functional

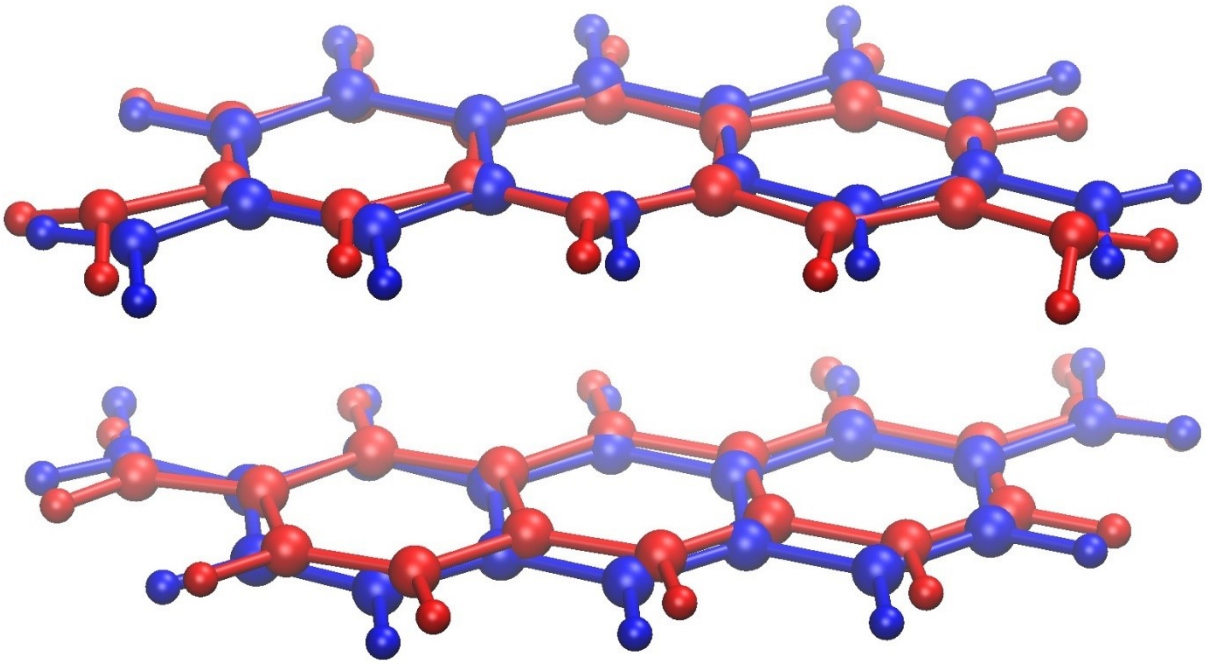

Fig. S14. Fitted structures of the proflavine dimer in the ground (blue) and excited (red) states, calculated using the PBE0 functional with GD3 correction

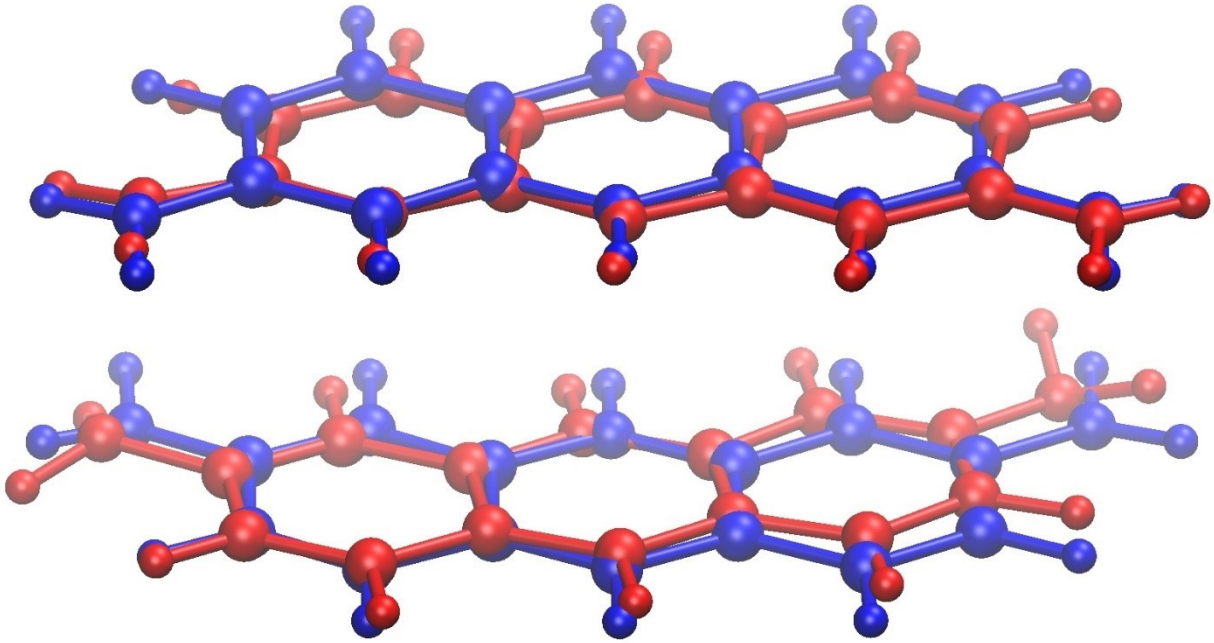

Fig. S15. Fitted structures of the proflavine dimer in the ground (blue) and excited (red) states, calculated using the PBE0 functional with GD3+BJ correction

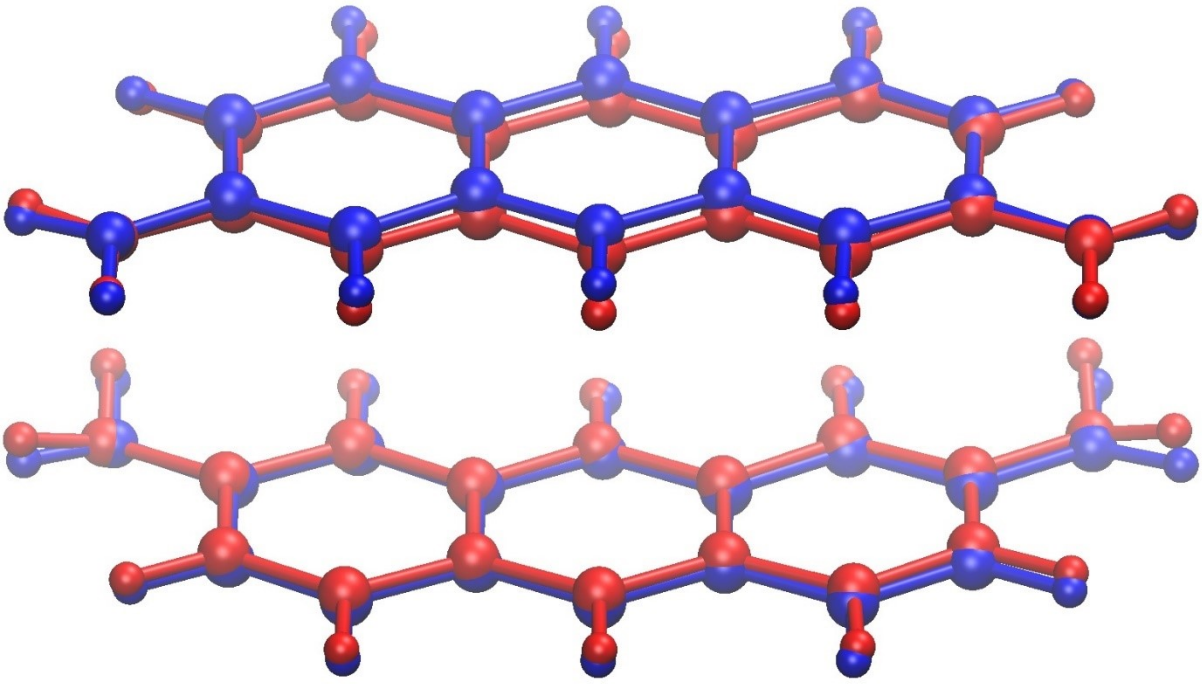

Fig. S16. Fitted structures of the proflavine dimer in the ground (blue) and excited (red) states, calculated using the PW6B95 functional with GD3 correction

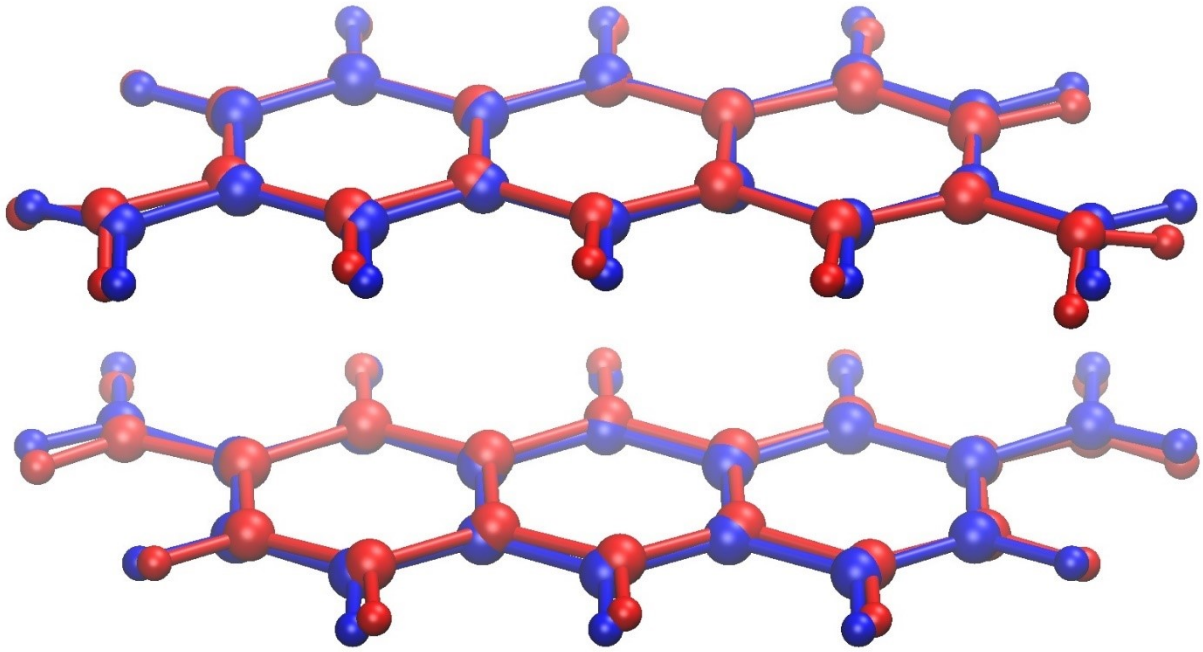

Fig. S17. Fitted structures of the proflavine dimer in the ground (blue) and excited (red) states, calculated using the PW6B95 functional with GD3+BJ correction

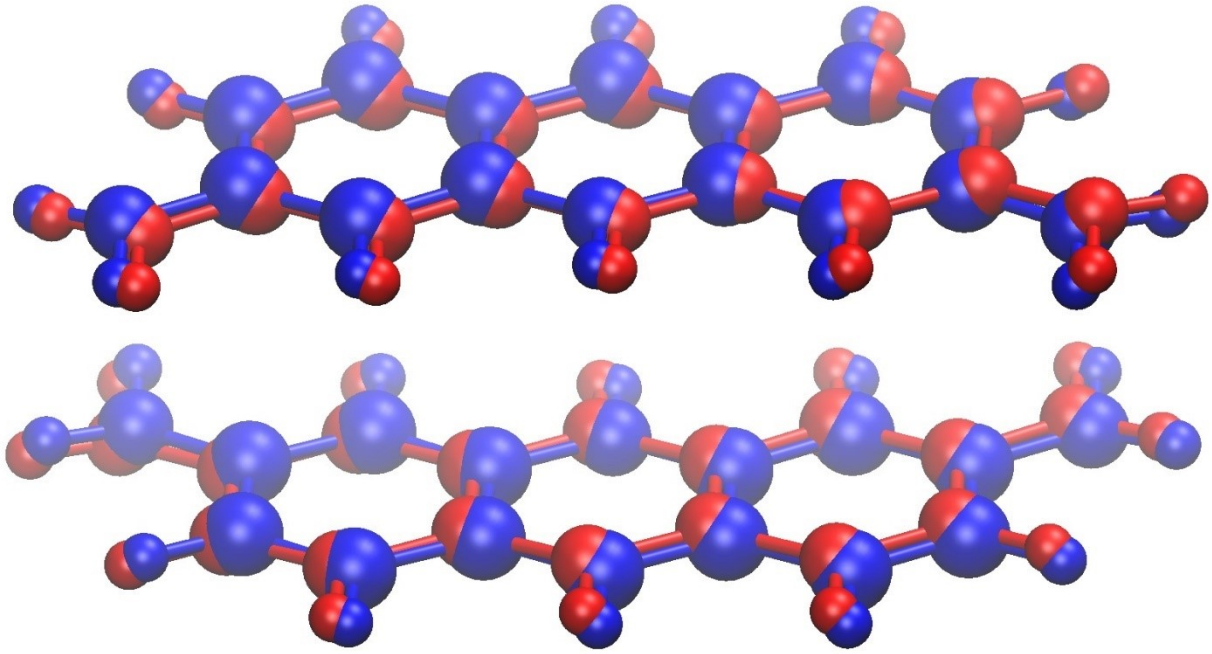

Fig. S18. Fitted structures of the proflavine dimer in the ground (blue) and excited (red) states, calculated using the ωB97XD functional

Table S1. NPA charges (*e*) of non-hydrogen atoms for free monomer (PF), molecules in a dimer (PF2_1 and PF2_2) in the ground (GS) and excited equilibrium (EES) states, and their changes (delta) due to excitation (delta) and dimerization (deltaGS) obtained through APFD functional

Atom	PF			PF2_1			PF2_2			deltaGS	deltaGS
	GS	EES	delta	GS	EES	delta	GS	EES	delta	(PF2_1-PF)	(PF2_2-PF)
C1	-0.021	-0.002	0.019	-0.533	-0.533	0.000	-0.533	-0.533	0.000	-0.513	-0.512
C2	0.445	0.449	0.004	-0.125	-0.125	0.000	-0.128	-0.128	0.000	-0.570	-0.572
C3	-0.599	-0.562	0.037	0.260	0.260	0.000	0.262	0.262	0.000	0.859	0.861
N3	-0.512	-0.510	0.002	-0.517	-0.517	0.000	-0.517	-0.517	0.000	-0.005	-0.005
C4	-0.668	-0.697	-0.028	-0.329	-0.329	0.000	-0.329	-0.329	0.000	0.339	0.340
C5	-0.668	-0.697	-0.028	-0.328	-0.328	0.000	-0.327	-0.327	0.000	0.340	0.341
C6	-0.598	-0.562	0.036	0.248	0.248	0.000	0.257	0.257	0.000	0.846	0.855
N6	-0.512	-0.510	0.002	-0.515	-0.515	0.000	-0.517	-0.517	0.000	-0.003	-0.005
C7	0.444	0.449	0.005	-0.122	-0.122	0.000	-0.128	-0.128	0.000	-0.566	-0.573
C8	-0.021	-0.002	0.019	-0.532	-0.532	0.000	-0.534	-0.534	0.000	-0.511	-0.513
C9	0.520	0.479	-0.041	0.036	0.036	0.000	0.035	0.035	0.000	-0.484	-0.485
N10	-0.110	-0.117	-0.007	-0.289	-0.289	0.000	-0.288	-0.288	0.000	-0.178	-0.178
C11	0.674	0.687	0.013	0.420	0.420	0.000	0.422	0.422	0.000	-0.253	-0.252
C12	-0.601	-0.625	-0.024	-0.218	-0.218	0.000	-0.219	-0.219	0.000	0.383	0.381
C13	-0.601	-0.625	-0.024	-0.211	-0.211	0.000	-0.213	-0.213	0.000	0.390	0.388
C14	0.674	0.687	0.013	0.418	0.418	0.000	0.421	0.421	0.000	-0.255	-0.253

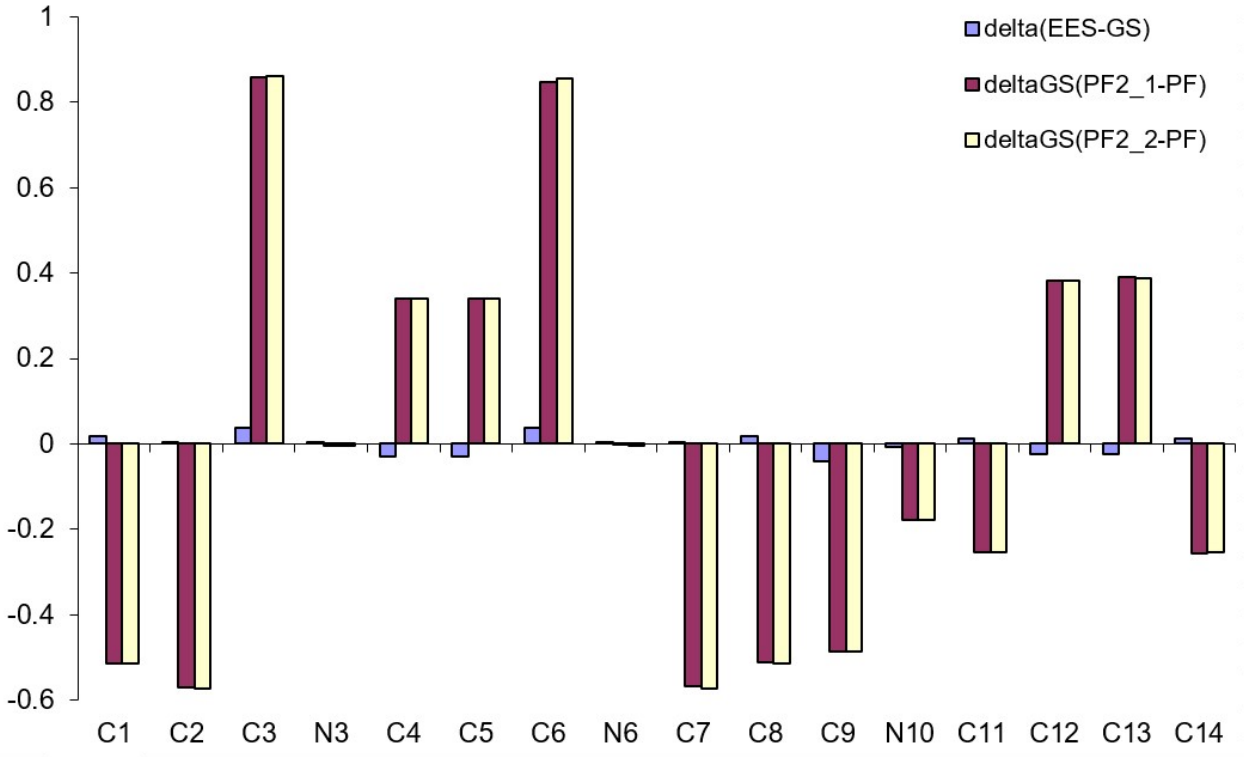

Fig. S19. Changes of NPA charges from Table S1

Table S2. NPA charges (*e*) obtained through B2PLYP functional with GD2 correction

Atom	PF GS	PF2_1 GS	PF2_2 GS	deltaGS (PF2_1-PF)	deltaGS (PF2_2-PF)
C1	-0.023	-0.060	-0.102	-0.037	-0.079
C2	0.334	0.093	0.124	-0.241	-0.210
C3	-0.408	-0.203	-0.220	0.205	0.187
N3	-0.536	-0.452	-0.451	0.085	0.086
C4	-0.581	0.010	0.059	0.591	0.640
C5	-0.581	0.047	0.034	0.628	0.615
C6	-0.408	-0.197	-0.237	0.211	0.171
N6	-0.536	-0.450	-0.447	0.086	0.090
C7	0.334	0.053	0.130	-0.281	-0.204
C8	-0.023	-0.064	-0.083	-0.041	-0.060
C9	0.490	-0.688	-0.660	-1.179	-1.150
N10	-0.234	-0.201	-0.239	0.033	-0.004
C11	0.526	0.208	0.121	-0.318	-0.405
C12	-0.441	-0.319	-0.222	0.122	0.219
C13	-0.441	-0.219	-0.128	0.222	0.313
C14	0.526	0.191	0.085	-0.335	-0.441

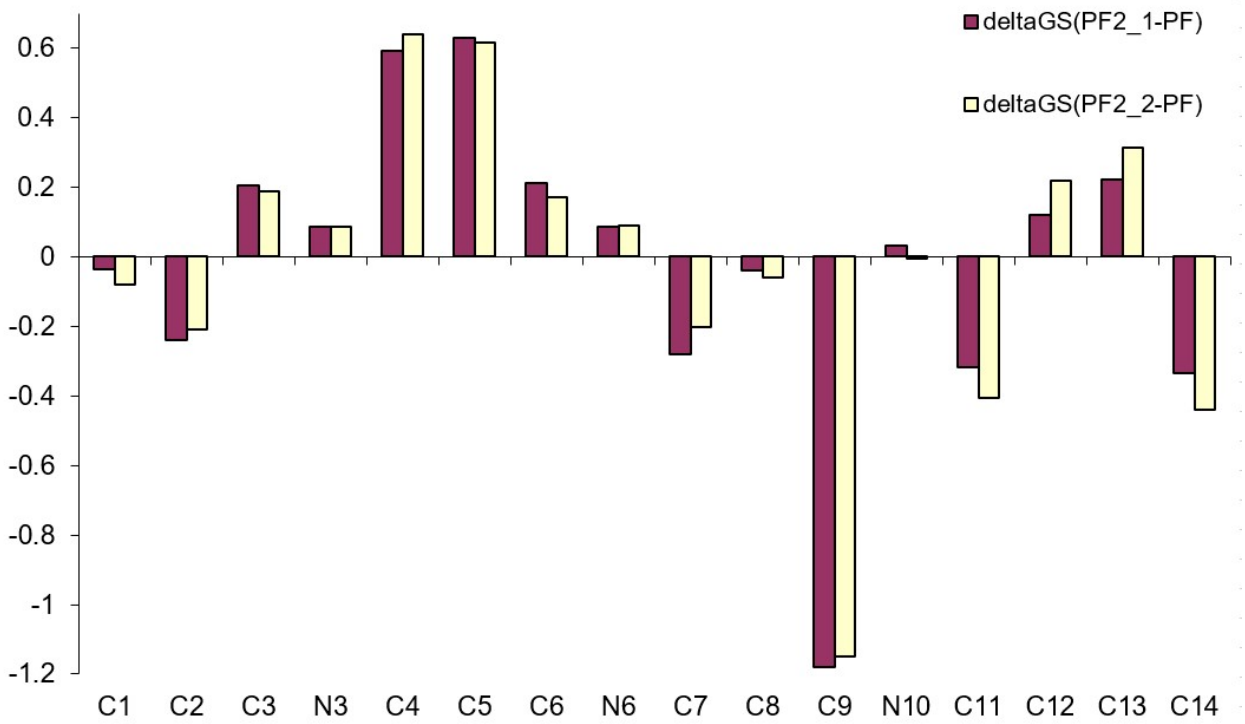

Fig. S20. Changes of NPA charges from Table S2

Table S3. NPA charges (*e*) obtained through B2PLYP functional with GD3 correction

Atom	PF GS	PF2_1 GS	PF2_2 GS	deltaGS (PF2_1-PF)	deltaGS (PF2_2-PF)
C1	-0.023	-0.487	-0.486	-0.464	-0.463
C2	0.334	-0.061	-0.074	-0.395	-0.408
C3	-0.408	0.213	0.234	0.621	0.641
N3	-0.536	-0.531	-0.536	0.005	0.001
C4	-0.581	-0.331	-0.331	0.250	0.251
C5	-0.581	-0.330	-0.330	0.251	0.251
C6	-0.408	0.221	0.227	0.629	0.635
N6	-0.536	-0.533	-0.534	0.003	0.002
C7	0.334	-0.064	-0.071	-0.398	-0.405
C8	-0.023	-0.487	-0.486	-0.464	-0.463
C9	0.490	0.168	0.166	-0.322	-0.324
N10	-0.234	-0.353	-0.354	-0.119	-0.120
C11	0.526	0.468	0.467	-0.058	-0.059
C12	-0.441	-0.264	-0.267	0.177	0.174
C13	-0.441	-0.264	-0.264	0.176	0.177
C14	0.526	0.466	0.466	-0.060	-0.060

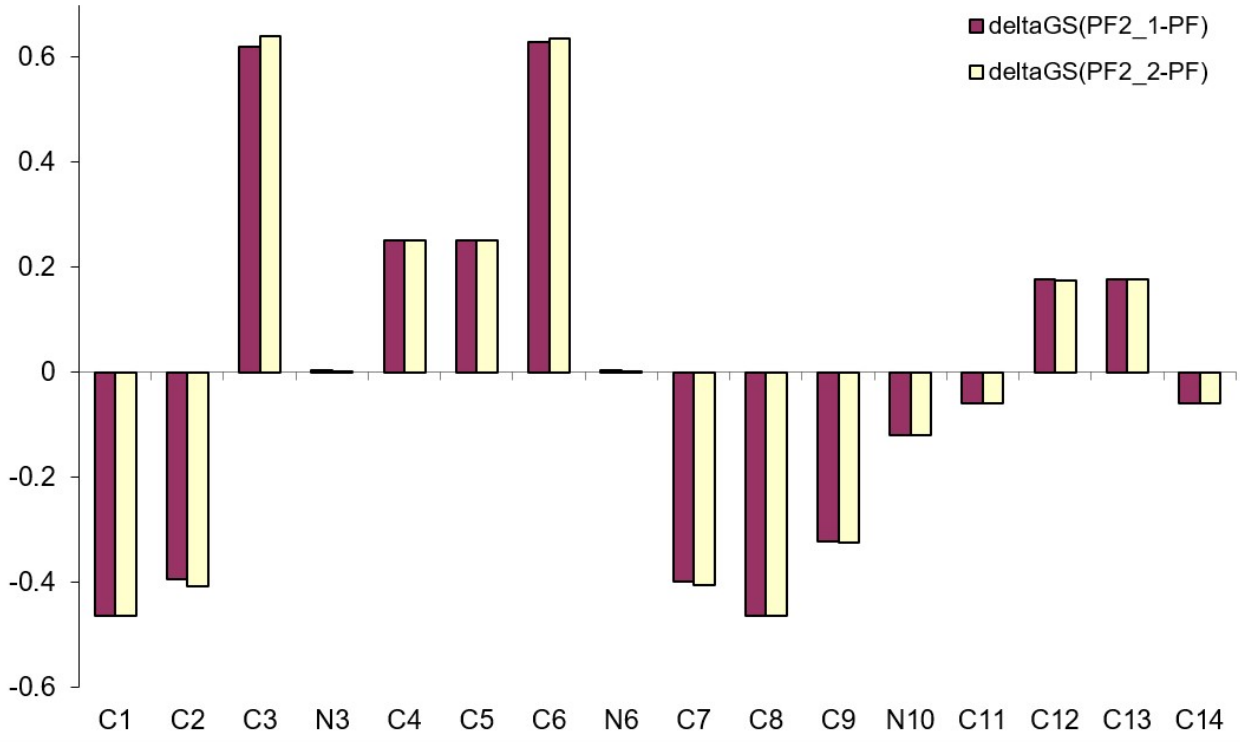

Fig. S21. Changes of NPA charges from Table S3

Table S4. NPA charges (*e*) obtained through B2PLYP functional with GD3+BJ correction

Atom	PF GS	PF2_1 GS	PF2_2 GS	deltaGS (PF2_1-PF)	deltaGS (PF2_2-PF)
C1	-0.023	-0.486	-0.486	-0.463	-0.463
C2	0.334	-0.067	-0.067	-0.401	-0.400
C3	-0.408	0.223	0.223	0.631	0.631
N3	-0.536	-0.534	-0.534	0.003	0.003
C4	-0.581	-0.330	-0.330	0.251	0.251
C5	-0.581	-0.330	-0.330	0.251	0.251
C6	-0.408	0.223	0.223	0.631	0.631
N6	-0.536	-0.533	-0.534	0.003	0.003
C7	0.334	-0.067	-0.067	-0.401	-0.400
C8	-0.023	-0.486	-0.486	-0.463	-0.463
C9	0.490	0.166	0.165	-0.325	-0.325
N10	-0.234	-0.354	-0.354	-0.120	-0.120
C11	0.526	0.466	0.466	-0.060	-0.060
C12	-0.441	-0.264	-0.264	0.177	0.177
C13	-0.441	-0.264	-0.264	0.177	0.177
C14	0.526	0.466	0.466	-0.060	-0.060

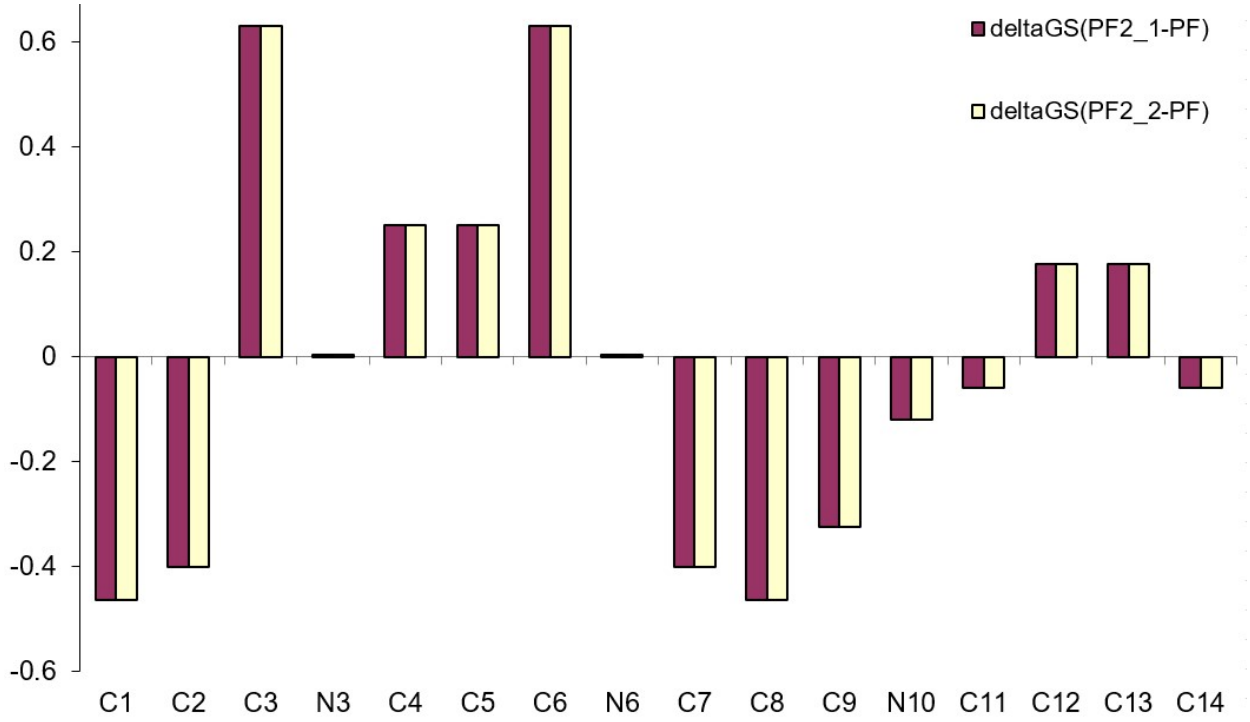

Fig. S22. Changes of NPA charges from Table S4

Table S5. NPA charges (*e*) obtained through B3LYP functional with GD2 correction

Atom	PF			PF2_1			PF2_2			deltaGS	deltaGS
	GS	EES	delta	GS	EES	delta	GS	EES	delta	(PF2_1-PF)	(PF2_2-PF)
C1	-0.064	0.016	0.080	-0.516	-0.386	0.130	-0.516	-0.404	0.112	-0.452	-0.452
C2	0.403	0.322	-0.081	-0.152	-0.190	-0.038	-0.151	-0.201	-0.050	-0.555	-0.554
C3	-0.427	-0.255	0.172	0.426	0.439	0.013	0.424	0.443	0.019	0.853	0.851
N3	-0.465	-0.532	-0.067	-0.518	-0.510	0.008	-0.518	-0.505	0.013	-0.053	-0.053
C4	-0.688	-0.670	0.018	-0.360	-0.317	0.043	-0.360	-0.294	0.065	0.327	0.328
C5	-0.641	-0.670	-0.029	-0.356	-0.306	0.051	-0.356	-0.286	0.070	0.284	0.284
C6	-0.423	-0.255	0.168	0.401	0.165	-0.236	0.398	0.134	-0.264	0.824	0.821
N6	-0.461	-0.532	-0.071	-0.513	-0.462	0.052	-0.513	-0.453	0.060	-0.052	-0.052
C7	0.327	0.322	-0.005	-0.138	0.051	0.190	-0.137	0.080	0.217	-0.465	-0.464
C8	-0.059	0.016	0.075	-0.516	-0.406	0.110	-0.516	-0.373	0.143	-0.457	-0.457
C9	0.432	0.470	0.037	0.128	-0.181	-0.309	0.128	-0.143	-0.271	-0.304	-0.304
N10	-0.260	-0.178	0.082	-0.301	-0.407	-0.106	-0.301	-0.382	-0.081	-0.041	-0.041
C11	0.547	0.562	0.015	0.369	0.288	-0.080	0.369	0.293	-0.076	-0.179	-0.178
C12	-0.314	-0.512	-0.198	-0.166	-0.115	0.052	-0.166	-0.143	0.022	0.148	0.149
C13	-0.262	-0.512	-0.250	-0.159	-0.004	0.155	-0.159	-0.053	0.106	0.103	0.103
C14	0.532	0.562	0.030	0.364	0.310	-0.054	0.364	0.255	-0.109	-0.168	-0.168

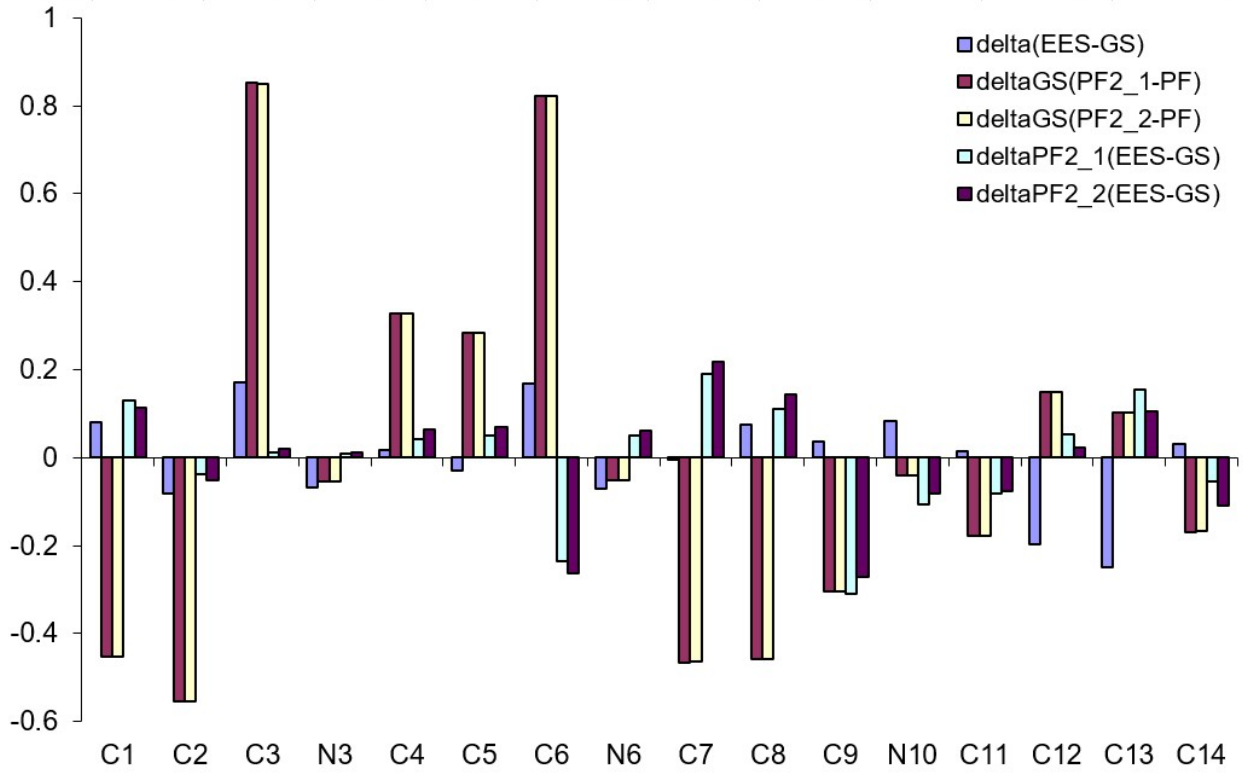

Fig. S23. Changes of NPA charges from Table S5

Table S6. NPA charges (*e*) obtained through B3LYP functional with GD3 correction

Atom	PF			PF2_1			PF2_2			deltaGS	deltaGS
	GS	EES	delta	GS	EES	delta	GS	EES	delta	(PF2_1-PF)	(PF2_2-PF)
C1	-0.064	0.019	0.083	-0.448	-0.461	-0.013	-0.446	-0.461	-0.015	-0.384	-0.382
C2	0.403	0.321	-0.081	-0.051	-0.092	-0.040	-0.064	-0.089	-0.026	-0.454	-0.466
C3	-0.427	-0.248	0.179	0.265	0.341	0.076	0.284	0.336	0.052	0.692	0.711
N3	-0.465	-0.534	-0.069	-0.489	-0.508	-0.019	-0.492	-0.507	-0.014	-0.024	-0.027
C4	-0.688	-0.671	0.016	-0.401	-0.378	0.023	-0.401	-0.378	0.023	0.287	0.287
C5	-0.641	-0.672	-0.031	-0.400	-0.377	0.023	-0.400	-0.378	0.021	0.241	0.241
C6	-0.423	-0.247	0.176	0.272	0.330	0.058	0.277	0.334	0.056	0.695	0.700
N6	-0.461	-0.534	-0.073	-0.490	-0.506	-0.016	-0.491	-0.506	-0.015	-0.029	-0.030
C7	0.327	0.321	-0.006	-0.054	-0.086	-0.031	-0.061	-0.086	-0.025	-0.382	-0.388
C8	-0.059	0.019	0.078	-0.448	-0.461	-0.013	-0.446	-0.461	-0.015	-0.389	-0.387
C9	0.432	0.469	0.037	0.201	0.111	-0.090	0.199	0.111	-0.088	-0.232	-0.233
N10	-0.260	-0.179	0.082	-0.271	-0.264	0.006	-0.271	-0.264	0.007	-0.011	-0.011
C11	0.547	0.558	0.011	0.511	0.461	-0.050	0.510	0.462	-0.048	-0.036	-0.037
C12	-0.314	-0.514	-0.200	-0.343	-0.280	0.062	-0.346	-0.280	0.066	-0.028	-0.031
C13	-0.262	-0.514	-0.252	-0.343	-0.279	0.065	-0.343	-0.280	0.063	-0.081	-0.081
C14	0.532	0.558	0.026	0.509	0.460	-0.050	0.509	0.460	-0.049	-0.022	-0.022

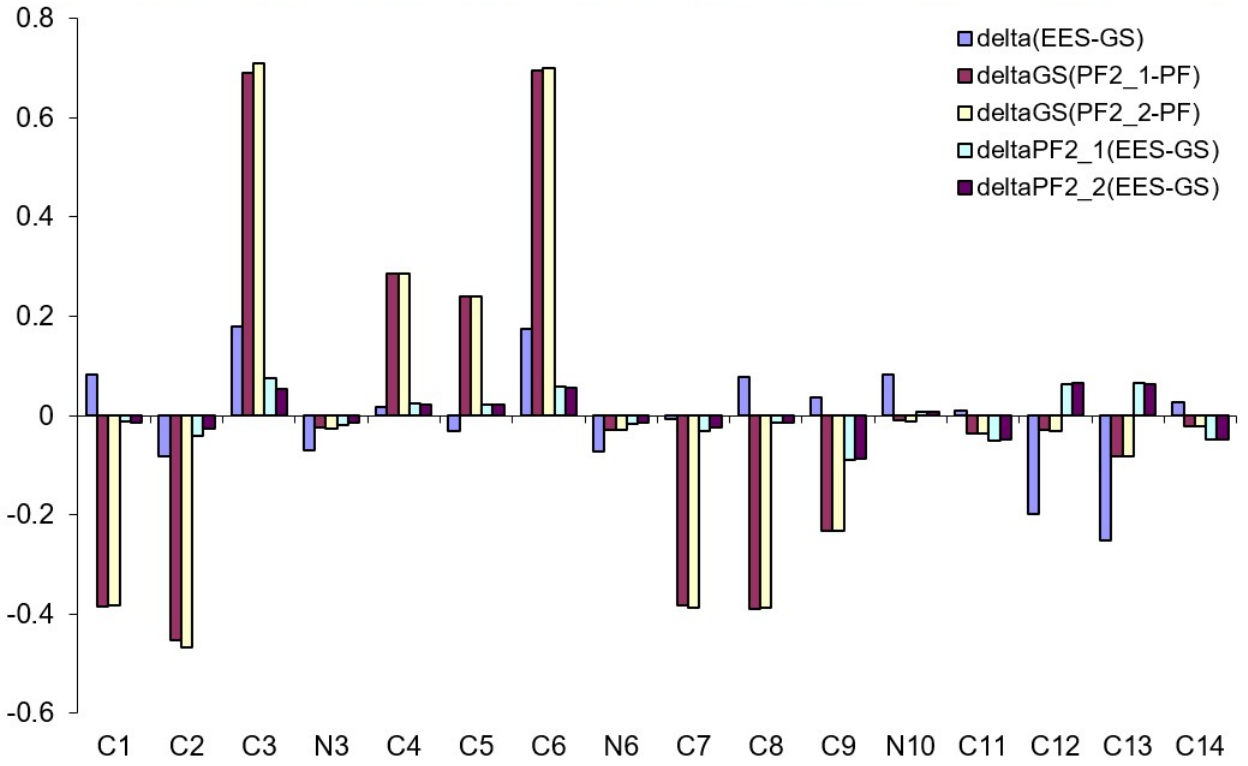

Fig. S24. Changes of NPA charges from Table S6

Table S7. NPA charges (*e*) obtained through B3LYP functional with GD3+BJ correction

Atom	PF			PF2_1			PF2_2			deltaGS	deltaGS
	GS	EES	delta	GS	EES	delta	GS	EES	delta	(PF2_1-PF)	(PF2_2-PF)
C1	-0.064	0.018	0.082	-0.448	-0.126	0.322	-0.446	-0.466	-0.020	-0.384	-0.382
C2	0.403	0.323	-0.079	-0.051	0.444	0.495	-0.064	-0.029	0.035	-0.454	-0.466
C3	-0.427	-0.253	0.174	0.265	-0.303	-0.568	0.284	0.019	-0.265	0.692	0.711
N3	-0.465	-0.533	-0.069	-0.489	-0.418	0.070	-0.492	-0.440	0.052	-0.024	-0.027
C4	-0.688	-0.672	0.016	-0.401	-0.190	0.211	-0.401	-0.245	0.155	0.287	0.287
C5	-0.641	-0.672	-0.032	-0.400	-0.290	0.110	-0.400	-0.233	0.166	0.241	0.241
C6	-0.423	-0.253	0.170	0.272	0.454	0.182	0.277	0.018	-0.260	0.695	0.700
N6	-0.461	-0.534	-0.072	-0.490	-0.500	-0.010	-0.491	-0.459	0.033	-0.029	-0.030
C7	0.327	0.323	-0.004	-0.054	-0.042	0.012	-0.061	-0.022	0.039	-0.382	-0.388
C8	-0.059	0.018	0.077	-0.448	-0.528	-0.080	-0.446	-0.067	0.379	-0.389	-0.387
C9	0.432	0.472	0.040	0.201	-0.109	-0.309	0.199	-0.169	-0.368	-0.232	-0.233
N10	-0.260	-0.179	0.082	-0.271	-0.188	0.083	-0.271	-0.218	0.053	-0.011	-0.011
C11	0.547	0.561	0.014	0.511	-0.199	-0.710	0.510	0.183	-0.327	-0.036	-0.037
C12	-0.314	-0.514	-0.200	-0.343	-0.122	0.221	-0.346	-0.086	0.259	-0.028	-0.031
C13	-0.262	-0.514	-0.252	-0.343	-0.201	0.142	-0.343	-0.208	0.135	-0.081	-0.081
C14	0.532	0.562	0.030	0.509	0.260	-0.250	0.509	0.380	-0.130	-0.022	-0.022

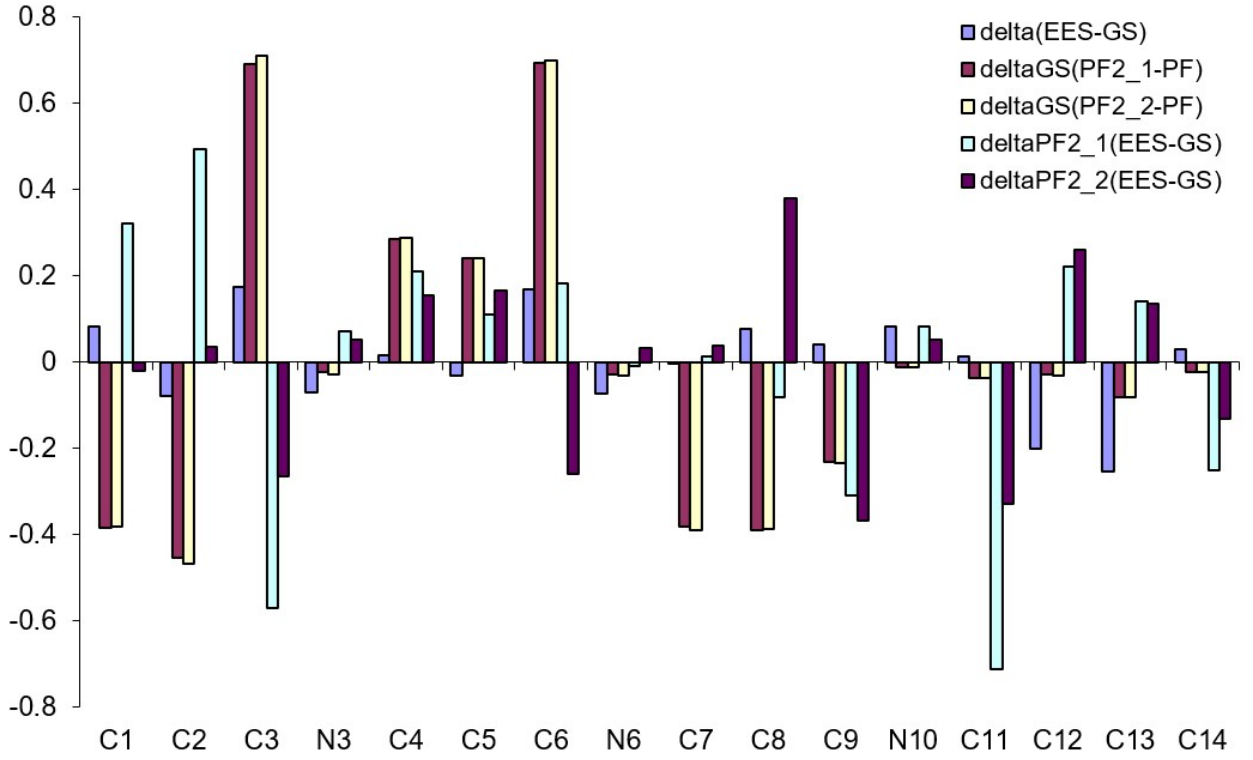

Fig. S25. Changes of NPA charges from Table S7

Table S8. NPA charges (*e*) obtained through B3PW91 functional with GD3 correction

Atom	PF			PF2_1			PF2_2			deltaGS	deltaGS
	GS	EES	delta	GS	EES	delta	GS	EES	delta	(PF2_1-PF)	(PF2_2-PF)
C1	-0.094	-0.006	0.088	-0.528	-0.508	0.020	-0.529	-0.508	0.020	-0.434	-0.435
C2	0.534	0.439	-0.094	-0.098	-0.078	0.020	-0.097	-0.078	0.018	-0.632	-0.630
C3	-0.774	-0.589	0.185	0.232	0.197	-0.035	0.230	0.199	-0.031	1.006	1.004
N3	-0.442	-0.508	-0.066	-0.505	-0.496	0.009	-0.504	-0.496	0.008	-0.062	-0.062
C4	-0.658	-0.648	0.010	-0.328	-0.333	-0.005	-0.328	-0.333	-0.005	0.330	0.330
C5	-0.607	-0.648	-0.041	-0.325	-0.328	-0.003	-0.325	-0.328	-0.003	0.282	0.282
C6	-0.769	-0.589	0.181	0.206	0.176	-0.030	0.203	0.171	-0.032	0.975	0.973
N6	-0.437	-0.508	-0.071	-0.499	-0.493	0.007	-0.499	-0.492	0.007	-0.062	-0.061
C7	0.445	0.439	-0.006	-0.083	-0.069	0.015	-0.082	-0.066	0.015	-0.528	-0.526
C8	-0.088	-0.006	0.081	-0.528	-0.509	0.018	-0.528	-0.509	0.019	-0.440	-0.441
C9	0.462	0.508	0.047	0.047	0.048	0.001	0.047	0.048	0.001	-0.414	-0.414
N10	-0.191	-0.108	0.083	-0.269	-0.273	-0.004	-0.270	-0.273	-0.004	-0.078	-0.079
C11	0.644	0.667	0.022	0.388	0.405	0.017	0.388	0.404	0.016	-0.257	-0.256
C12	-0.377	-0.590	-0.213	-0.175	-0.194	-0.018	-0.175	-0.193	-0.018	0.201	0.202
C13	-0.316	-0.589	-0.273	-0.167	-0.184	-0.017	-0.167	-0.184	-0.017	0.149	0.149
C14	0.633	0.667	0.034	0.383	0.401	0.019	0.383	0.401	0.018	-0.250	-0.250

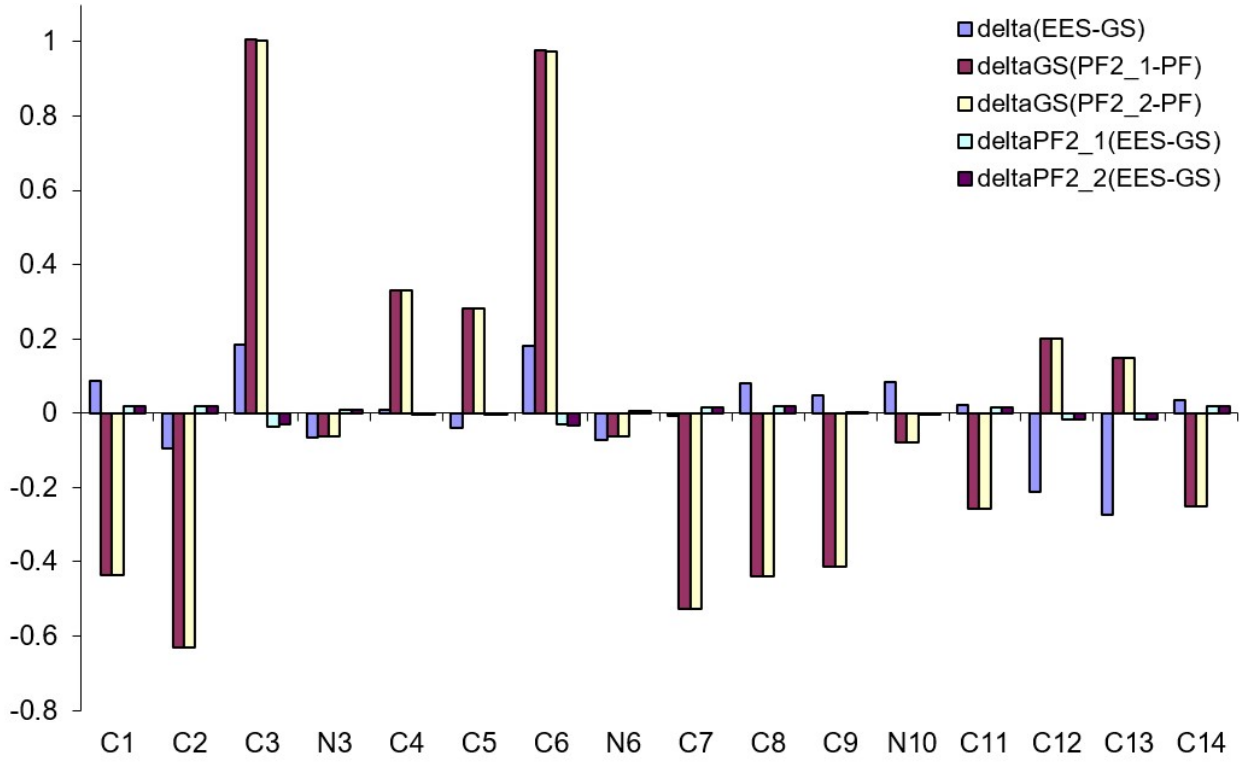

Fig. S26. Changes of NPA charges from Table S8

Table S9. NPA charges (*e*) obtained through B3PW91 functional with GD3+BJ correction

Atom	PF			PF2_1			PF2_2			deltaGS	deltaGS
	GS	EES	delta	GS	EES	delta	GS	EES	delta	(PF2_1-PF)	(PF2_2-PF)
C1	-0.094	-0.007	0.086	-0.523	-0.501	0.022	-0.522	-0.499	0.023	-0.429	-0.428
C2	0.534	0.442	-0.092	-0.047	-0.086	-0.039	-0.037	-0.078	-0.041	-0.581	-0.571
C3	-0.774	-0.595	0.179	0.161	0.202	0.041	0.146	0.190	0.043	0.935	0.920
N3	-0.442	-0.508	-0.065	-0.502	-0.497	0.005	-0.499	-0.495	0.004	-0.060	-0.057
C4	-0.658	-0.649	0.009	-0.330	-0.321	0.009	-0.331	-0.322	0.009	0.328	0.327
C5	-0.607	-0.649	-0.042	-0.330	-0.320	0.010	-0.330	-0.320	0.010	0.277	0.276
C6	-0.769	-0.595	0.175	0.140	0.183	0.043	0.142	0.182	0.040	0.909	0.911
N6	-0.437	-0.508	-0.070	-0.498	-0.494	0.004	-0.498	-0.494	0.005	-0.061	-0.061
C7	0.445	0.442	-0.003	-0.034	-0.075	-0.041	-0.033	-0.073	-0.039	-0.479	-0.478
C8	-0.088	-0.007	0.080	-0.521	-0.499	0.021	-0.522	-0.501	0.021	-0.433	-0.434
C9	0.462	0.512	0.051	0.007	0.035	0.028	0.008	0.036	0.028	-0.455	-0.454
N10	-0.191	-0.108	0.083	-0.236	-0.280	-0.044	-0.237	-0.281	-0.044	-0.046	-0.046
C11	0.644	0.670	0.025	0.523	0.417	-0.106	0.522	0.417	-0.105	-0.122	-0.123
C12	-0.377	-0.589	-0.212	-0.284	-0.210	0.074	-0.282	-0.209	0.073	0.093	0.095
C13	-0.316	-0.589	-0.273	-0.281	-0.207	0.073	-0.281	-0.206	0.074	0.035	0.035
C14	0.633	0.670	0.037	0.520	0.415	-0.104	0.519	0.414	-0.105	-0.113	-0.114

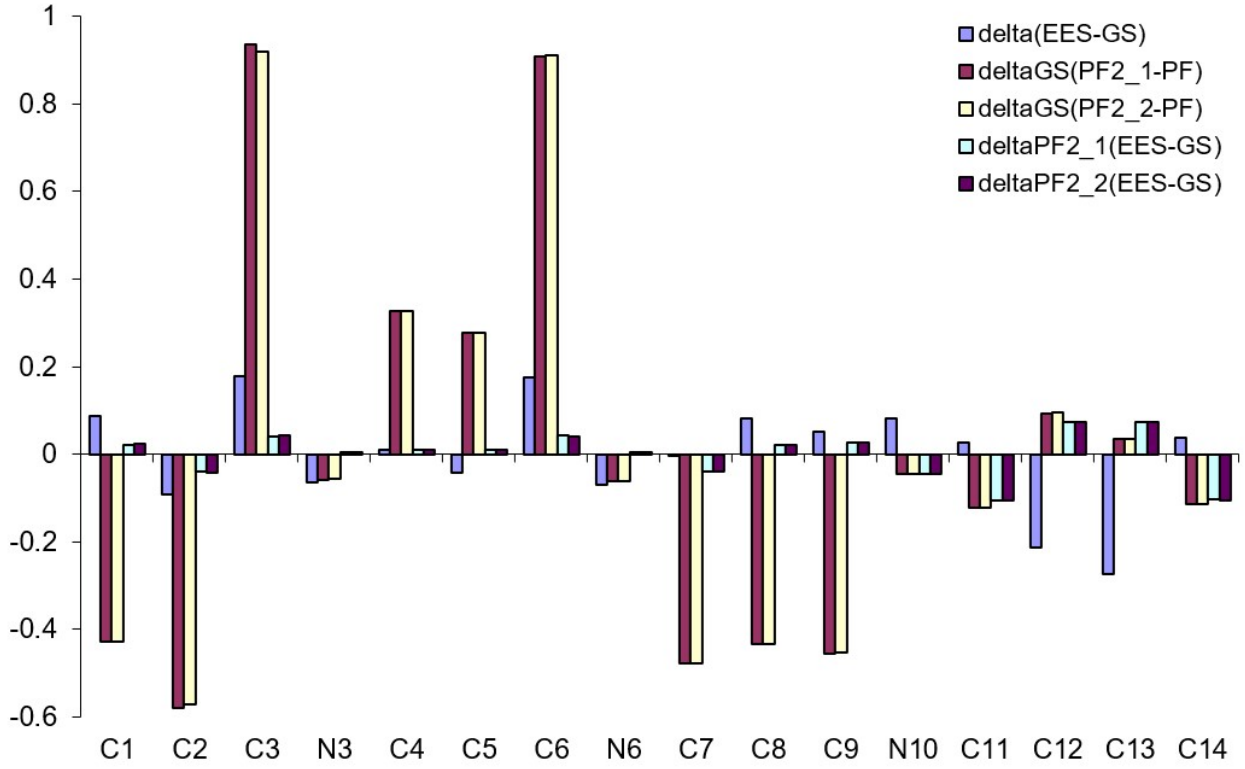

Fig. S27. Changes of NPA charges from Table S9

Table S10. NPA charges (*e*) obtained through BMK functional with GD3 correction

Atom	PF			PF2_1			PF2_2			deltaGS	deltaGS
	GS	EES	delta	GS	EES	delta	GS	EES	delta	(PF2_1-PF)	(PF2_2-PF)
C1	-0.045	0.038	0.084	-0.486	-0.363	0.124	-0.487	-0.353	0.134	-0.441	-0.442
C2	0.254	0.217	-0.037	-0.199	-0.142	0.057	-0.197	-0.121	0.077	-0.453	-0.452
C3	-0.219	-0.127	0.092	0.564	0.323	-0.241	0.562	0.310	-0.252	0.784	0.781
N3	-0.541	-0.596	-0.055	-0.599	-0.563	0.036	-0.599	-0.556	0.043	-0.058	-0.058
C4	-0.551	-0.530	0.020	-0.278	-0.239	0.040	-0.278	-0.265	0.013	0.272	0.273
C5	-0.513	-0.531	-0.018	-0.273	-0.247	0.026	-0.272	-0.221	0.051	0.240	0.241
C6	-0.208	-0.127	0.081	0.535	0.717	0.182	0.532	0.662	0.130	0.742	0.739
N6	-0.538	-0.596	-0.058	-0.593	-0.602	-0.008	-0.593	-0.594	-0.001	-0.055	-0.054
C7	0.196	0.217	0.021	-0.185	-0.148	0.037	-0.183	-0.123	0.060	-0.381	-0.380
C8	-0.034	0.038	0.072	-0.486	-0.497	-0.011	-0.486	-0.467	0.019	-0.452	-0.452
C9	0.317	0.347	0.029	0.236	0.212	-0.024	0.236	0.221	-0.016	-0.081	-0.081
N10	-0.341	-0.255	0.086	-0.466	-0.453	0.014	-0.467	-0.459	0.008	-0.125	-0.126
C11	0.490	0.515	0.026	0.338	0.247	-0.091	0.338	0.243	-0.095	-0.152	-0.152
C12	-0.273	-0.469	-0.196	-0.156	-0.022	0.134	-0.156	-0.045	0.111	0.117	0.117
C13	-0.240	-0.468	-0.229	-0.148	-0.369	-0.221	-0.147	-0.342	-0.195	0.092	0.093
C14	0.475	0.515	0.041	0.334	0.275	-0.059	0.334	0.246	-0.088	-0.141	-0.141

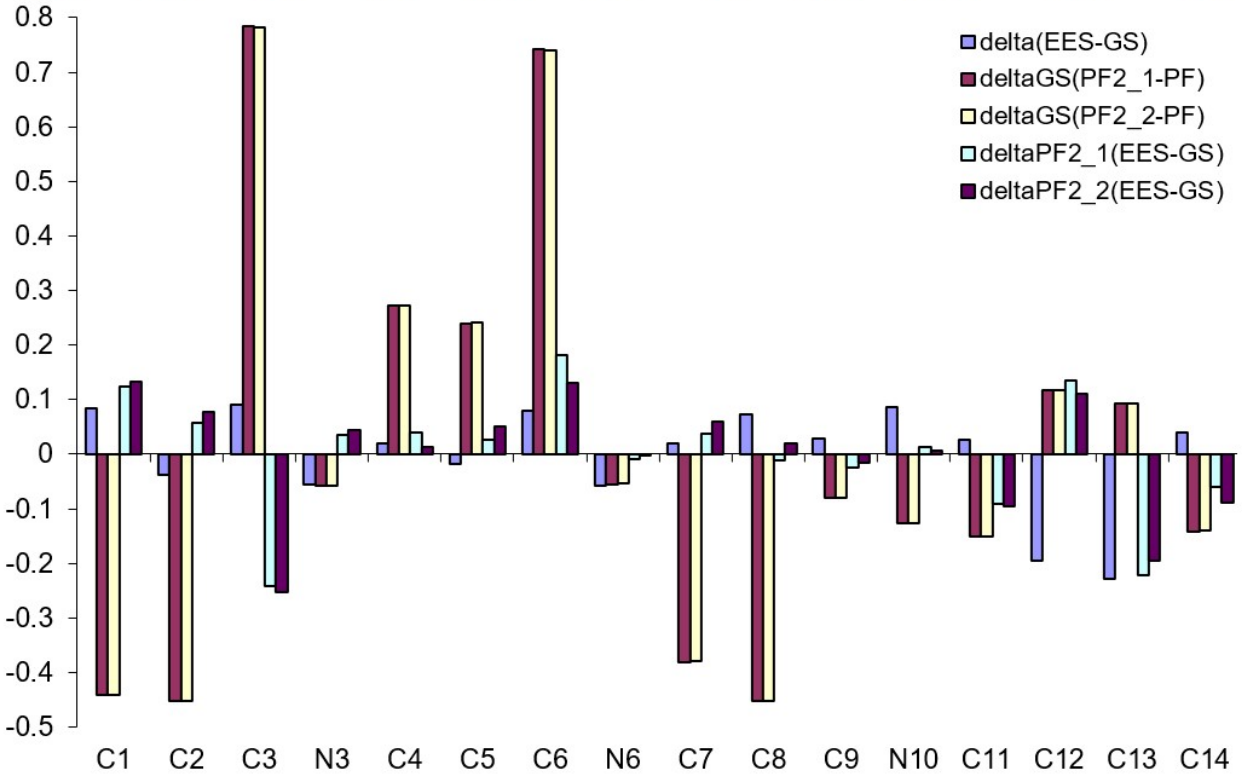

Fig. S28. Changes of NPA charges from Table S10

Table S11. NPA charges (*e*) obtained through BMK functional with GD3+BJ correction

Atom	PF			PF2_1			PF2_2			deltaGS	deltaGS
	GS	EES	delta	GS	EES	delta	GS	EES	delta	(PF2_1-PF)	(PF2_2-PF)
C1	-0.045	0.038	0.083	-0.440	-0.366	0.073	-0.440	-0.400	0.040	-0.394	-0.394
C2	0.254	0.219	-0.036	-0.132	-0.167	-0.035	-0.124	-0.151	-0.027	-0.386	-0.378
C3	-0.219	-0.132	0.087	0.430	0.511	0.080	0.417	0.500	0.083	0.649	0.636
N3	-0.541	-0.595	-0.054	-0.584	-0.587	-0.003	-0.581	-0.585	-0.003	-0.043	-0.040
C4	-0.551	-0.530	0.021	-0.257	-0.193	0.063	-0.256	-0.195	0.061	0.294	0.295
C5	-0.513	-0.530	-0.017	-0.254	-0.194	0.061	-0.256	-0.168	0.088	0.258	0.257
C6	-0.208	-0.131	0.076	0.410	0.508	0.098	0.412	0.476	0.064	0.617	0.619
N6	-0.538	-0.595	-0.057	-0.580	-0.585	-0.005	-0.581	-0.583	-0.002	-0.042	-0.042
C7	0.196	0.218	0.022	-0.121	-0.152	-0.030	-0.121	-0.135	-0.015	-0.318	-0.317
C8	-0.034	0.038	0.072	-0.438	-0.387	0.051	-0.440	-0.377	0.063	-0.404	-0.406
C9	0.317	0.348	0.031	0.189	0.155	-0.033	0.190	0.146	-0.044	-0.128	-0.127
N10	-0.341	-0.255	0.086	-0.426	-0.451	-0.025	-0.426	-0.449	-0.023	-0.085	-0.085
C11	0.490	0.518	0.029	0.357	0.340	-0.017	0.357	0.345	-0.012	-0.133	-0.132
C12	-0.273	-0.470	-0.197	-0.177	-0.323	-0.147	-0.175	-0.295	-0.120	0.096	0.098
C13	-0.240	-0.470	-0.230	-0.173	-0.322	-0.149	-0.173	-0.316	-0.143	0.066	0.067
C14	0.475	0.518	0.044	0.355	0.352	-0.003	0.355	0.327	-0.028	-0.119	-0.120

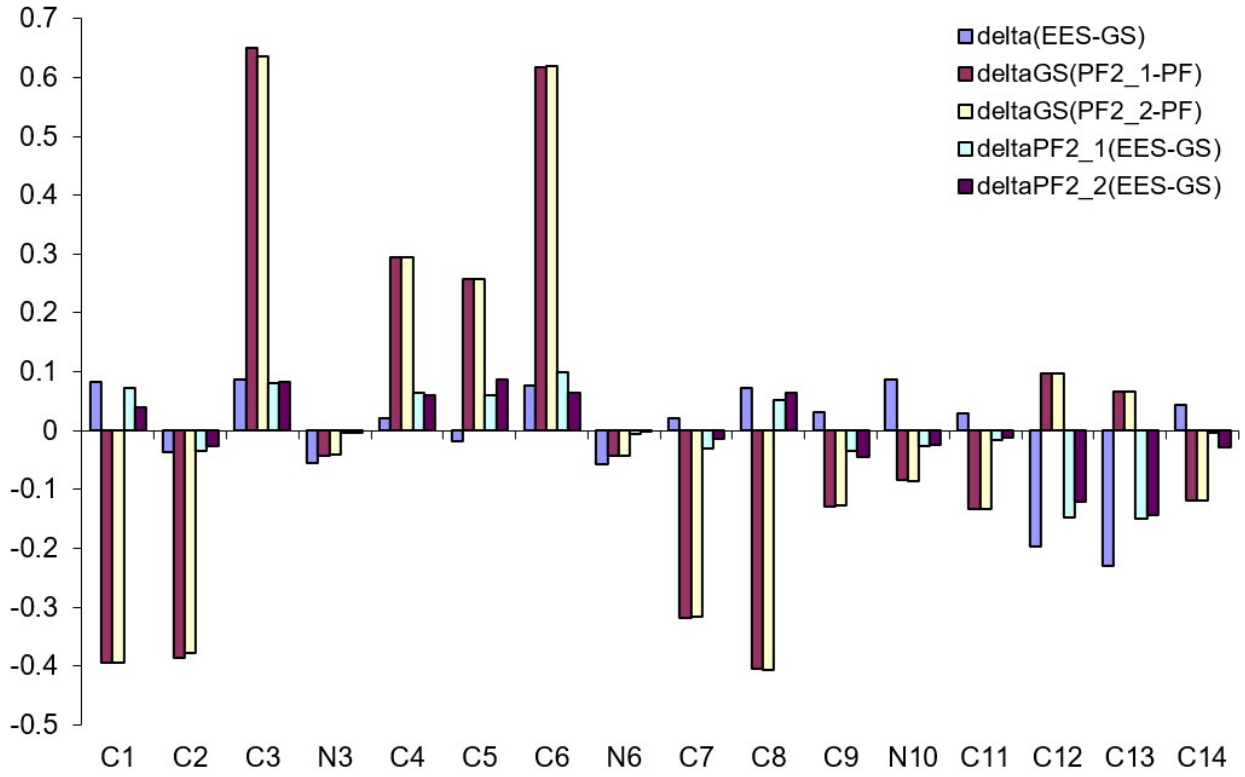

Fig. S29. Changes of NPA charges from Table S11

Table S12. NPA charges (*e*) obtained through CAM-B3LYP functional with GD3 correction

Atom	PF			PF2_1			PF2_2			deltaGS	deltaGS
	GS	EES	delta	GS	EES	delta	GS	EES	delta	(PF2_1-PF)	(PF2_2-PF)
C1	-0.081	-0.006	0.075	-0.472	-0.485	-0.013	-0.471	-0.484	-0.013	-0.391	-0.390
C2	0.336	0.292	-0.044	-0.157	-0.149	0.008	-0.147	-0.145	0.002	-0.492	-0.483
C3	-0.341	-0.196	0.145	0.405	0.398	-0.007	0.391	0.393	0.001	0.746	0.732
N3	-0.493	-0.567	-0.074	-0.542	-0.544	-0.002	-0.539	-0.543	-0.004	-0.049	-0.047
C4	-0.683	-0.684	-0.001	-0.363	-0.370	-0.008	-0.363	-0.371	-0.007	0.320	0.319
C5	-0.634	-0.684	-0.049	-0.363	-0.370	-0.007	-0.363	-0.371	-0.008	0.272	0.271
C6	-0.335	-0.195	0.139	0.385	0.387	0.003	0.387	0.387	0.001	0.719	0.721
N6	-0.489	-0.567	-0.077	-0.538	-0.542	-0.004	-0.539	-0.542	-0.003	-0.049	-0.049
C7	0.262	0.292	0.031	-0.144	-0.142	0.002	-0.143	-0.142	0.001	-0.406	-0.405
C8	-0.077	-0.006	0.071	-0.470	-0.484	-0.014	-0.471	-0.485	-0.013	-0.393	-0.394
C9	0.426	0.473	0.047	0.144	0.157	0.013	0.145	0.158	0.013	-0.282	-0.281
N10	-0.292	-0.208	0.084	-0.291	-0.286	0.005	-0.291	-0.286	0.005	0.001	0.001
C11	0.495	0.522	0.028	0.430	0.423	-0.007	0.429	0.422	-0.007	-0.065	-0.066
C12	-0.281	-0.475	-0.195	-0.275	-0.254	0.021	-0.273	-0.253	0.019	0.006	0.008
C13	-0.237	-0.475	-0.239	-0.272	-0.252	0.019	-0.272	-0.252	0.020	-0.035	-0.035
C14	0.477	0.522	0.045	0.427	0.420	-0.006	0.426	0.421	-0.005	-0.050	-0.051

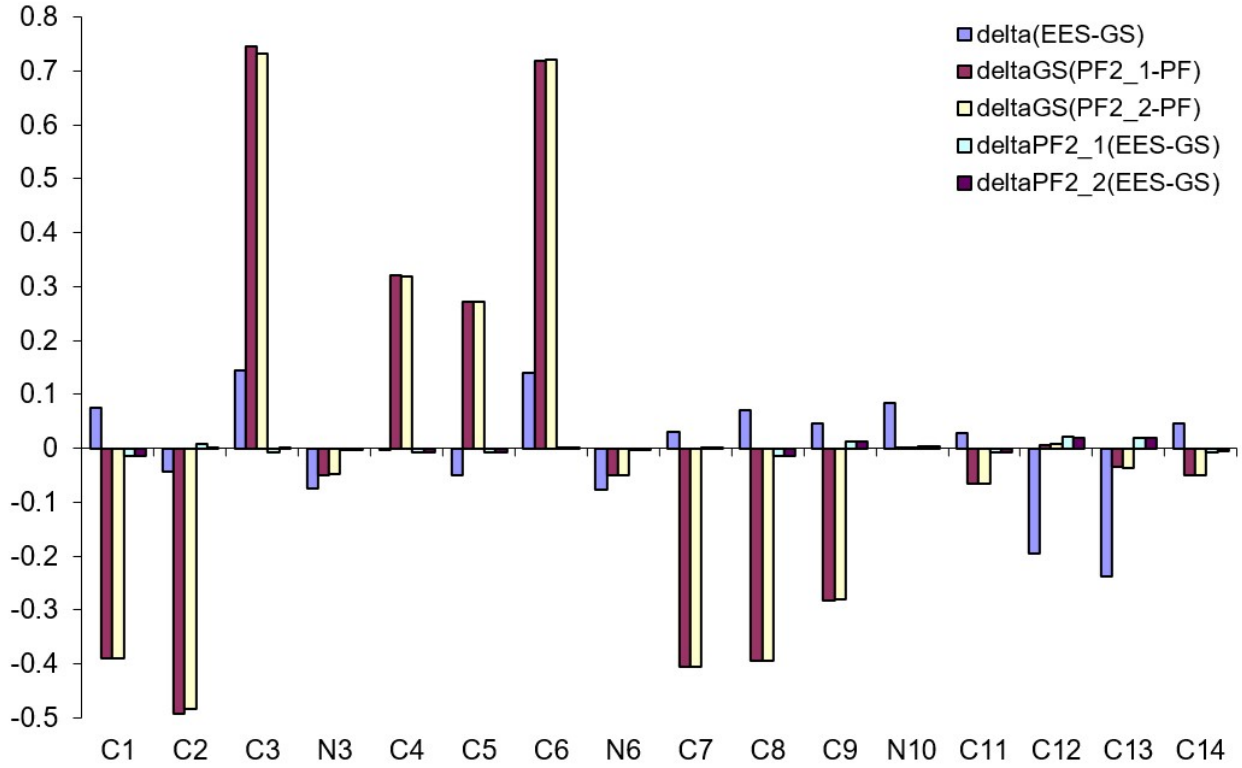

Fig. S30. Changes of NPA charges from Table S12

Table S13. NPA charges (*e*) obtained through CAM-B3LYP functional with GD3+BJ correction

Atom	PF			PF2_1			PF2_2			deltaGS	deltaGS
	GS	EES	delta	GS	EES	delta	GS	EES	delta	(PF2_1-PF)	(PF2_2-PF)
C1	-0.081	-0.006	0.075	-0.472	-0.460	0.012	-0.471	-0.460	0.011	-0.391	-0.390
C2	0.336	0.293	-0.043	-0.157	-0.150	0.007	-0.147	-0.142	0.005	-0.492	-0.483
C3	-0.341	-0.198	0.143	0.405	0.390	-0.015	0.391	0.380	-0.011	0.746	0.732
N3	-0.493	-0.566	-0.074	-0.542	-0.544	-0.001	-0.539	-0.542	-0.002	-0.049	-0.047
C4	-0.683	-0.683	0.000	-0.363	-0.362	0.001	-0.363	-0.362	0.001	0.320	0.319
C5	-0.634	-0.683	-0.049	-0.363	-0.362	0.000	-0.363	-0.362	0.001	0.272	0.271
C6	-0.335	-0.198	0.136	0.385	0.376	-0.009	0.387	0.377	-0.010	0.719	0.721
N6	-0.489	-0.566	-0.077	-0.538	-0.541	-0.003	-0.539	-0.541	-0.002	-0.049	-0.049
C7	0.262	0.293	0.031	-0.144	-0.139	0.005	-0.143	-0.138	0.005	-0.406	-0.405
C8	-0.077	-0.006	0.071	-0.470	-0.459	0.011	-0.471	-0.460	0.011	-0.393	-0.394
C9	0.426	0.474	0.048	0.144	0.127	-0.017	0.145	0.128	-0.017	-0.282	-0.281
N10	-0.292	-0.207	0.084	-0.291	-0.285	0.006	-0.291	-0.285	0.006	0.001	0.001
C11	0.495	0.524	0.029	0.430	0.408	-0.022	0.429	0.407	-0.022	-0.065	-0.066
C12	-0.281	-0.476	-0.195	-0.275	-0.250	0.025	-0.273	-0.249	0.024	0.006	0.008
C13	-0.237	-0.475	-0.239	-0.272	-0.249	0.023	-0.272	-0.250	0.022	-0.035	-0.035
C14	0.477	0.524	0.047	0.427	0.406	-0.021	0.426	0.406	-0.020	-0.050	-0.051

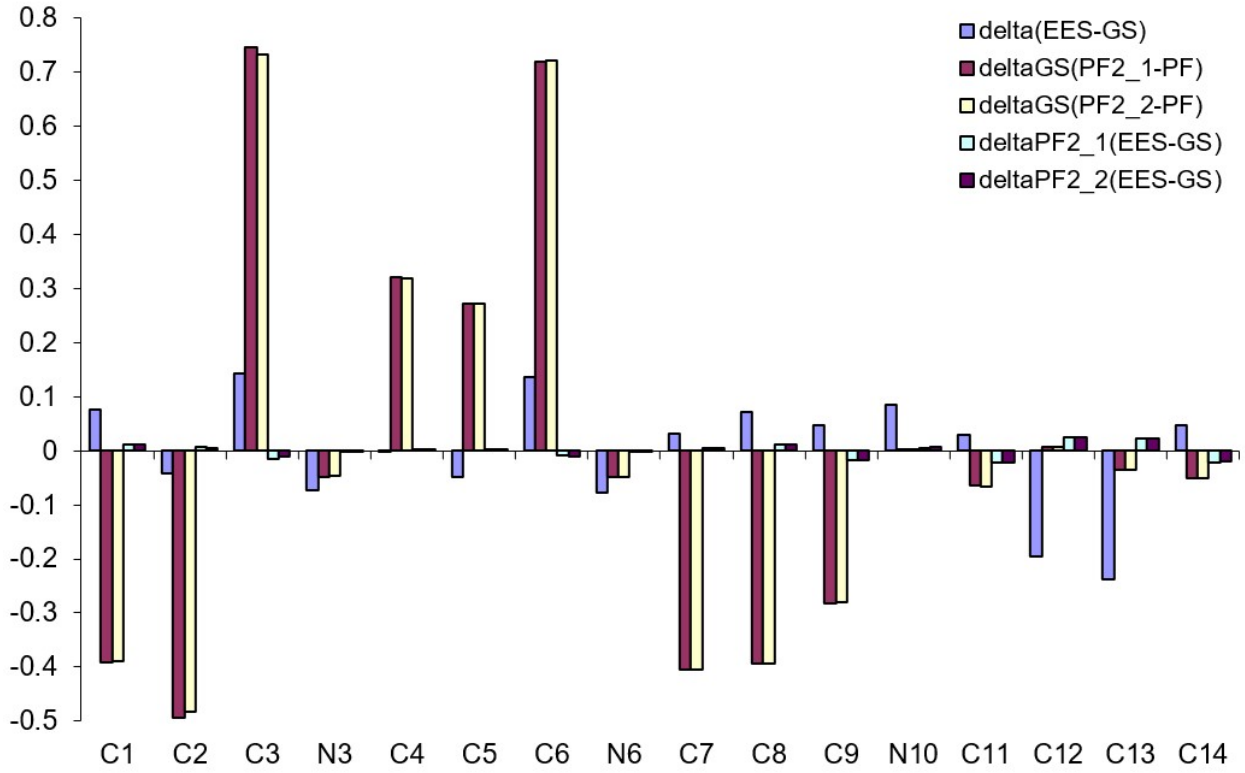

Fig. S31. Changes of NPA charges from Table S13

Table S14. NPA charges (*e*) obtained through M05 functional with GD3 correction

Atom	PF			PF2_1			PF2_2			deltaGS	deltaGS
	GS	EES	delta	GS	EES	delta	GS	EES	delta	(PF2_1-PF)	(PF2_2-PF)
C1	-0.048	0.027	0.075	-0.514	-0.089	0.425	-0.514	-0.426	0.087	-0.467	-0.466
C2	0.490	0.411	-0.079	-0.126	0.152	0.278	-0.117	-0.098	0.019	-0.616	-0.607
C3	-0.488	-0.322	0.166	0.528	-0.166	-0.694	0.513	0.347	-0.166	1.016	1.001
N3	-0.480	-0.530	-0.050	-0.551	-0.408	0.143	-0.548	-0.508	0.040	-0.071	-0.068
C4	-0.766	-0.738	0.028	-0.431	-0.226	0.205	-0.431	-0.315	0.116	0.335	0.335
C5	-0.717	-0.738	-0.022	-0.430	-0.313	0.117	-0.431	-0.262	0.169	0.286	0.286
C6	-0.481	-0.321	0.160	0.507	0.192	-0.315	0.509	-0.096	-0.605	0.988	0.990
N6	-0.477	-0.530	-0.054	-0.547	-0.469	0.078	-0.548	-0.482	0.065	-0.070	-0.071
C7	0.403	0.411	0.008	-0.114	0.061	0.174	-0.113	-0.004	0.109	-0.517	-0.516
C8	-0.045	0.027	0.072	-0.512	-0.448	0.065	-0.514	-0.036	0.478	-0.467	-0.469
C9	0.393	0.446	0.053	-0.003	-0.321	-0.318	-0.002	-0.440	-0.438	-0.396	-0.395
N10	-0.250	-0.168	0.081	-0.326	-0.151	0.176	-0.327	-0.194	0.133	-0.077	-0.077
C11	0.465	0.465	-0.001	0.317	-0.015	-0.332	0.317	0.035	-0.282	-0.148	-0.148
C12	-0.319	-0.519	-0.200	-0.223	-0.159	0.064	-0.221	-0.192	0.030	0.096	0.098
C13	-0.256	-0.519	-0.263	-0.220	-0.194	0.026	-0.220	0.040	0.260	0.036	0.036
C14	0.451	0.465	0.014	0.315	0.136	-0.178	0.314	0.221	-0.093	-0.136	-0.137

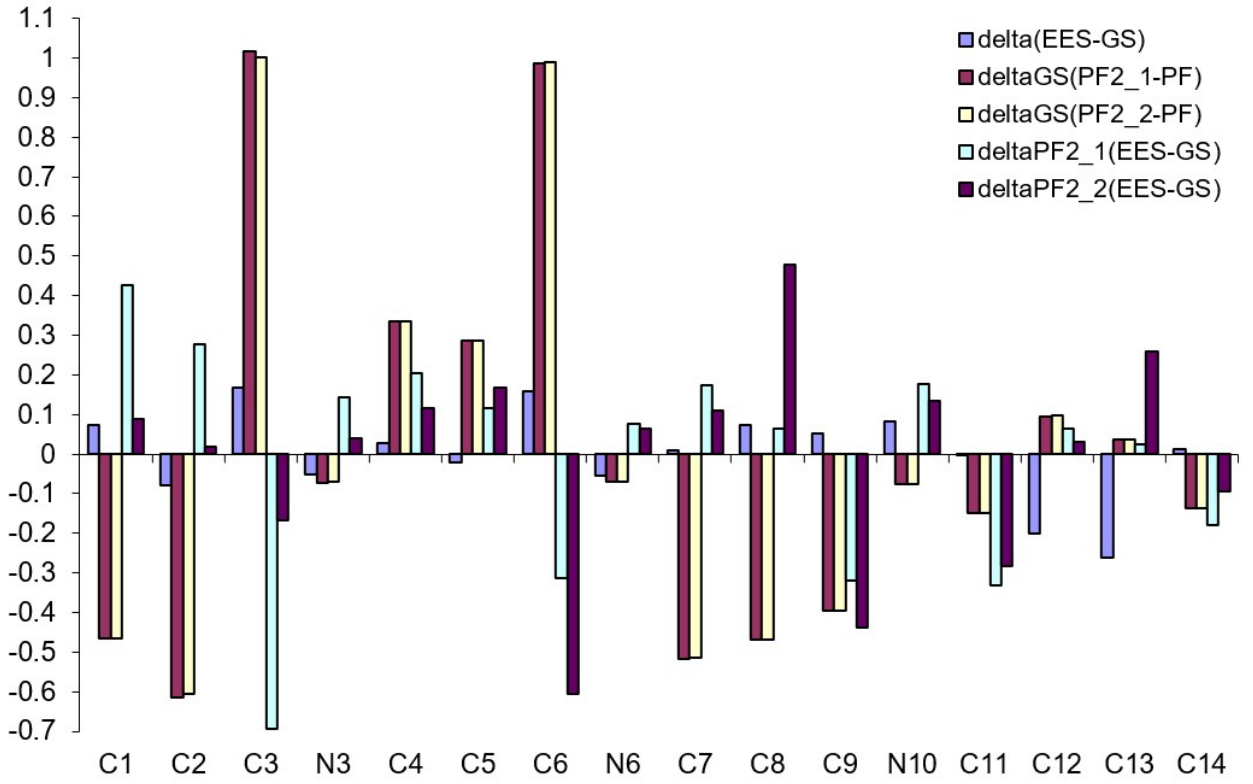

Fig. S32. Changes of NPA charges from Table S14

Table S15. NPA charges (*e*) obtained through M052X functional

Atom	PF			PF2_1			PF2_2			deltaGS	deltaGS
	GS	EES	delta	GS	EES	delta	GS	EES	delta	(PF2_1-PF)	(PF2_2-PF)
C1	-0.118	-0.050	0.068	-0.515	-0.512	0.003	-0.515	-0.438	0.076	-0.398	-0.397
C2	0.357	0.307	-0.050	-0.175	-0.152	0.023	-0.165	-0.066	0.098	-0.532	-0.522
C3	-0.485	-0.321	0.163	0.356	0.354	-0.003	0.342	0.311	-0.031	0.841	0.827
N3	-0.473	-0.545	-0.072	-0.529	-0.506	0.022	-0.526	-0.502	0.024	-0.056	-0.053
C4	-0.678	-0.686	-0.009	-0.343	-0.334	0.009	-0.344	-0.339	0.005	0.335	0.334
C5	-0.623	-0.686	-0.063	-0.343	-0.337	0.007	-0.344	-0.361	-0.018	0.280	0.280
C6	-0.472	-0.321	0.151	0.335	0.326	-0.009	0.337	0.442	0.105	0.807	0.809
N6	-0.470	-0.545	-0.075	-0.525	-0.508	0.016	-0.525	-0.520	0.005	-0.055	-0.056
C7	0.273	0.307	0.034	-0.162	-0.112	0.050	-0.161	-0.211	-0.050	-0.434	-0.433
C8	-0.111	-0.050	0.061	-0.514	-0.435	0.079	-0.515	-0.508	0.007	-0.402	-0.404
C9	0.542	0.592	0.049	0.222	0.152	-0.070	0.223	0.156	-0.067	-0.321	-0.320
N10	-0.232	-0.150	0.083	-0.244	-0.285	-0.041	-0.245	-0.282	-0.037	-0.012	-0.012
C11	0.563	0.611	0.048	0.469	0.375	-0.094	0.468	0.307	-0.161	-0.094	-0.095
C12	-0.350	-0.563	-0.213	-0.344	-0.276	0.067	-0.342	-0.282	0.060	0.006	0.009
C13	-0.309	-0.563	-0.254	-0.340	-0.248	0.092	-0.340	-0.276	0.064	-0.031	-0.031
C14	0.551	0.611	0.060	0.466	0.308	-0.158	0.466	0.377	-0.088	-0.086	-0.086

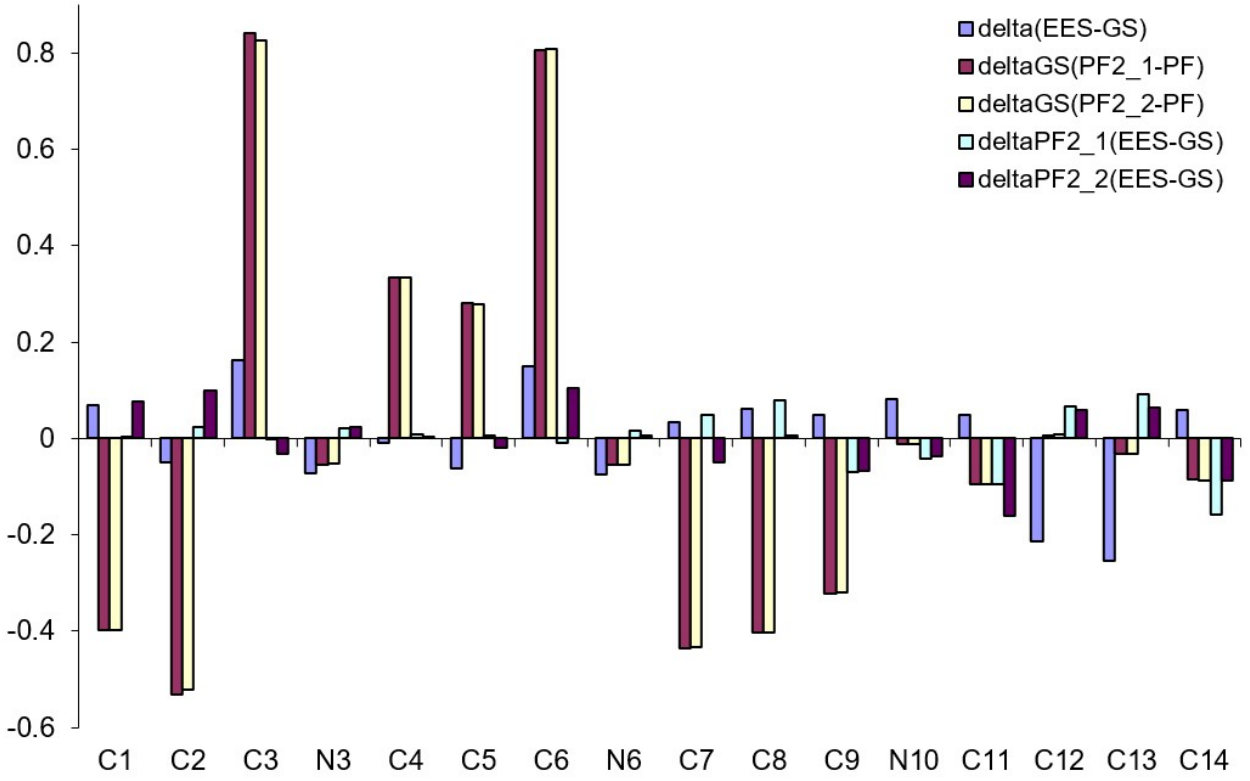

Fig. S33. Changes of NPA charges from Table S15

Table S16. NPA charges (*e*) obtained through M06 functional

Atom	PF			PF2_1			PF2_2			deltaGS	deltaGS
	GS	EES	delta	GS	EES	delta	GS	EES	delta	(PF2_1-PF)	(PF2_2-PF)
C1	0.001	0.052	0.050	-0.395	-0.437	-0.043	-0.394	-0.437	-0.043	-0.396	-0.395
C2	0.450	0.428	-0.022	0.065	0.062	-0.003	0.075	0.067	-0.008	-0.385	-0.375
C3	-0.496	-0.368	0.128	0.101	0.118	0.017	0.088	0.111	0.023	0.598	0.584
N3	-0.468	-0.543	-0.075	-0.479	-0.483	-0.004	-0.476	-0.481	-0.006	-0.011	-0.007
C4	-0.430	-0.477	-0.047	-0.080	-0.105	-0.025	-0.081	-0.105	-0.024	0.350	0.349
C5	-0.387	-0.477	-0.090	-0.080	-0.105	-0.025	-0.081	-0.106	-0.025	0.307	0.306
C6	-0.486	-0.367	0.118	0.082	0.109	0.027	0.083	0.108	0.025	0.567	0.569
N6	-0.465	-0.544	-0.078	-0.475	-0.481	-0.006	-0.475	-0.481	-0.006	-0.009	-0.010
C7	0.379	0.428	0.048	0.078	0.069	-0.009	0.079	0.071	-0.008	-0.301	-0.301
C8	0.007	0.051	0.045	-0.393	-0.437	-0.044	-0.395	-0.438	-0.043	-0.400	-0.401
C9	0.233	0.348	0.115	-0.053	-0.006	0.047	-0.052	-0.006	0.046	-0.286	-0.285
N10	-0.253	-0.171	0.083	-0.244	-0.247	-0.003	-0.244	-0.247	-0.003	0.009	0.009
C11	0.423	0.469	0.046	0.309	0.338	0.028	0.308	0.337	0.029	-0.114	-0.115
C12	-0.346	-0.545	-0.198	-0.305	-0.297	0.008	-0.303	-0.296	0.007	0.041	0.043
C13	-0.311	-0.544	-0.234	-0.302	-0.296	0.005	-0.301	-0.295	0.006	0.009	0.009
C14	0.407	0.469	0.063	0.306	0.336	0.031	0.305	0.336	0.031	-0.101	-0.101

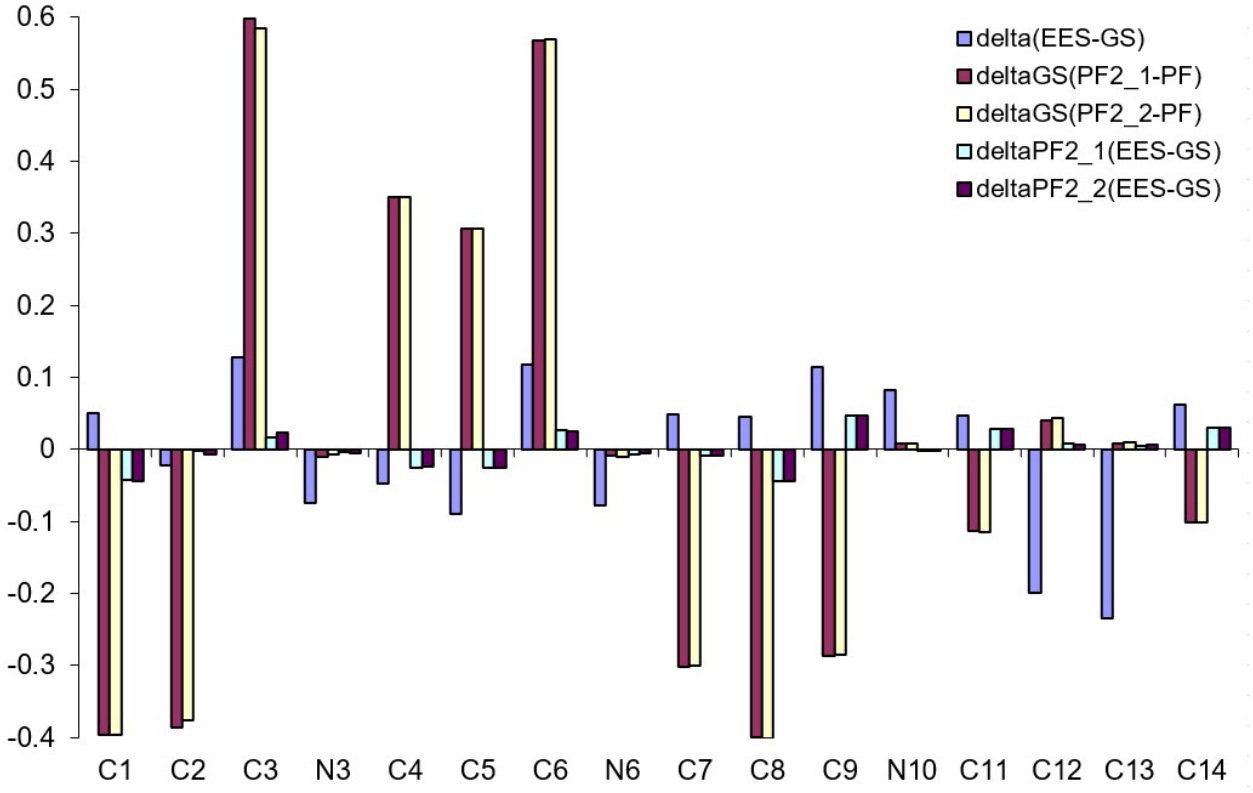

Fig. S34. Changes of NPA charges from Table S16

Table S17. NPA charges (*e*) obtained through M062X functional

Atom	PF			PF2_1			PF2_2			deltaGS	deltaGS
	GS	EES	delta	GS	EES	delta	GS	EES	delta	(PF2_1-PF)	(PF2_2-PF)
C1	-0.062	-0.006	0.056	-0.457	-0.507	-0.050	-0.456	-0.506	-0.050	-0.395	-0.394
C2	0.321	0.270	-0.051	-0.192	-0.273	-0.081	-0.182	-0.264	-0.082	-0.513	-0.503
C3	-0.413	-0.242	0.171	0.362	0.494	0.131	0.347	0.478	0.131	0.775	0.760
N3	-0.511	-0.587	-0.076	-0.556	-0.572	-0.016	-0.552	-0.569	-0.017	-0.045	-0.041
C4	-0.607	-0.630	-0.023	-0.291	-0.336	-0.045	-0.291	-0.334	-0.043	0.316	0.316
C5	-0.557	-0.630	-0.073	-0.290	-0.333	-0.043	-0.291	-0.334	-0.042	0.267	0.266
C6	-0.401	-0.242	0.160	0.339	0.471	0.132	0.341	0.467	0.127	0.740	0.742
N6	-0.507	-0.587	-0.080	-0.550	-0.568	-0.017	-0.551	-0.567	-0.016	-0.043	-0.044
C7	0.245	0.270	0.025	-0.179	-0.262	-0.083	-0.178	-0.257	-0.079	-0.424	-0.423
C8	-0.059	-0.007	0.052	-0.455	-0.507	-0.052	-0.457	-0.508	-0.052	-0.396	-0.398
C9	0.380	0.440	0.060	0.109	0.164	0.055	0.110	0.165	0.055	-0.271	-0.270
N10	-0.296	-0.212	0.084	-0.336	-0.379	-0.043	-0.336	-0.379	-0.043	-0.040	-0.040
C11	0.461	0.501	0.040	0.372	0.349	-0.022	0.371	0.349	-0.022	-0.089	-0.090
C12	-0.318	-0.515	-0.197	-0.276	-0.204	0.071	-0.274	-0.202	0.072	0.042	0.044
C13	-0.285	-0.514	-0.229	-0.272	-0.198	0.074	-0.272	-0.198	0.074	0.014	0.014
C14	0.450	0.501	0.051	0.369	0.348	-0.021	0.369	0.348	-0.021	-0.081	-0.081

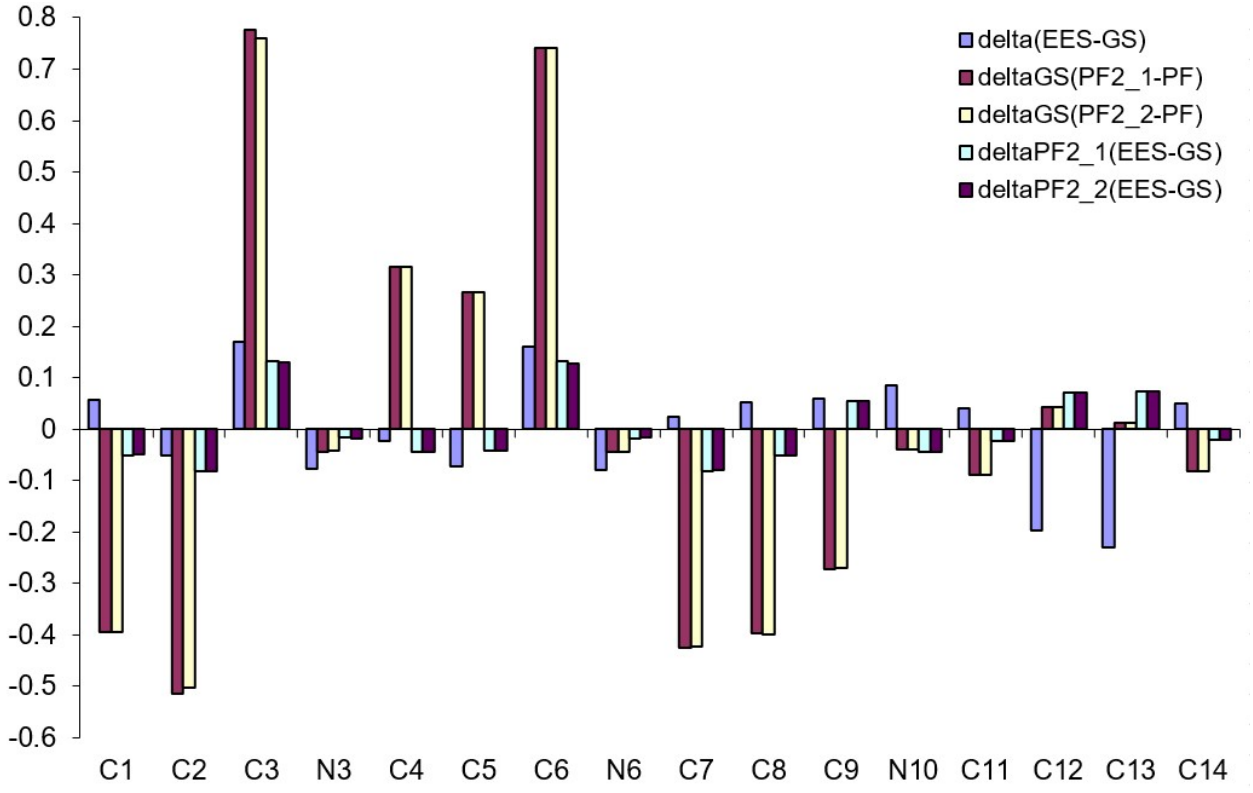

Fig. S35. Changes of NPA charges from Table S17

Table S18. NPA charges (*e*) obtained through M06HF functional

Atom	PF			PF2_1			PF2_2			deltaGS	deltaGS
	GS	EES	delta	GS	EES	delta	GS	EES	delta	(PF2_1-PF)	(PF2_2-PF)
C1	-0.079	0.028	0.106	-0.546	-0.595	-0.049	-0.545	-0.594	-0.049	-0.467	-0.466
C2	0.646	0.460	-0.186	-0.227	-0.324	-0.097	-0.214	-0.319	-0.105	-0.873	-0.860
C3	-0.962	-0.607	0.355	0.393	0.502	0.109	0.375	0.495	0.119	1.355	1.337
N3	-0.545	-0.622	-0.077	-0.610	-0.617	-0.007	-0.606	-0.616	-0.010	-0.065	-0.060
C4	-0.860	-0.873	-0.013	-0.456	-0.457	-0.001	-0.458	-0.457	0.001	0.403	0.402
C5	-0.778	-0.873	-0.095	-0.457	-0.456	0.001	-0.457	-0.457	0.001	0.321	0.321
C6	-0.926	-0.606	0.321	0.366	0.490	0.124	0.367	0.488	0.120	1.292	1.294
N6	-0.544	-0.622	-0.078	-0.604	-0.615	-0.011	-0.604	-0.614	-0.010	-0.059	-0.060
C7	0.524	0.459	-0.065	-0.210	-0.319	-0.108	-0.209	-0.316	-0.106	-0.735	-0.734
C8	-0.091	0.027	0.118	-0.543	-0.593	-0.050	-0.544	-0.594	-0.050	-0.453	-0.454
C9	0.613	0.621	0.008	0.068	0.100	0.032	0.069	0.101	0.032	-0.545	-0.544
N10	-0.180	-0.096	0.084	-0.259	-0.290	-0.031	-0.259	-0.290	-0.031	-0.079	-0.079
C11	0.554	0.684	0.130	0.401	0.334	-0.067	0.400	0.333	-0.067	-0.153	-0.154
C12	-0.435	-0.810	-0.375	-0.450	-0.344	0.106	-0.449	-0.343	0.106	-0.015	-0.013
C13	-0.387	-0.809	-0.422	-0.446	-0.341	0.105	-0.446	-0.341	0.105	-0.059	-0.058
C14	0.533	0.684	0.152	0.397	0.333	-0.065	0.397	0.333	-0.064	-0.135	-0.136

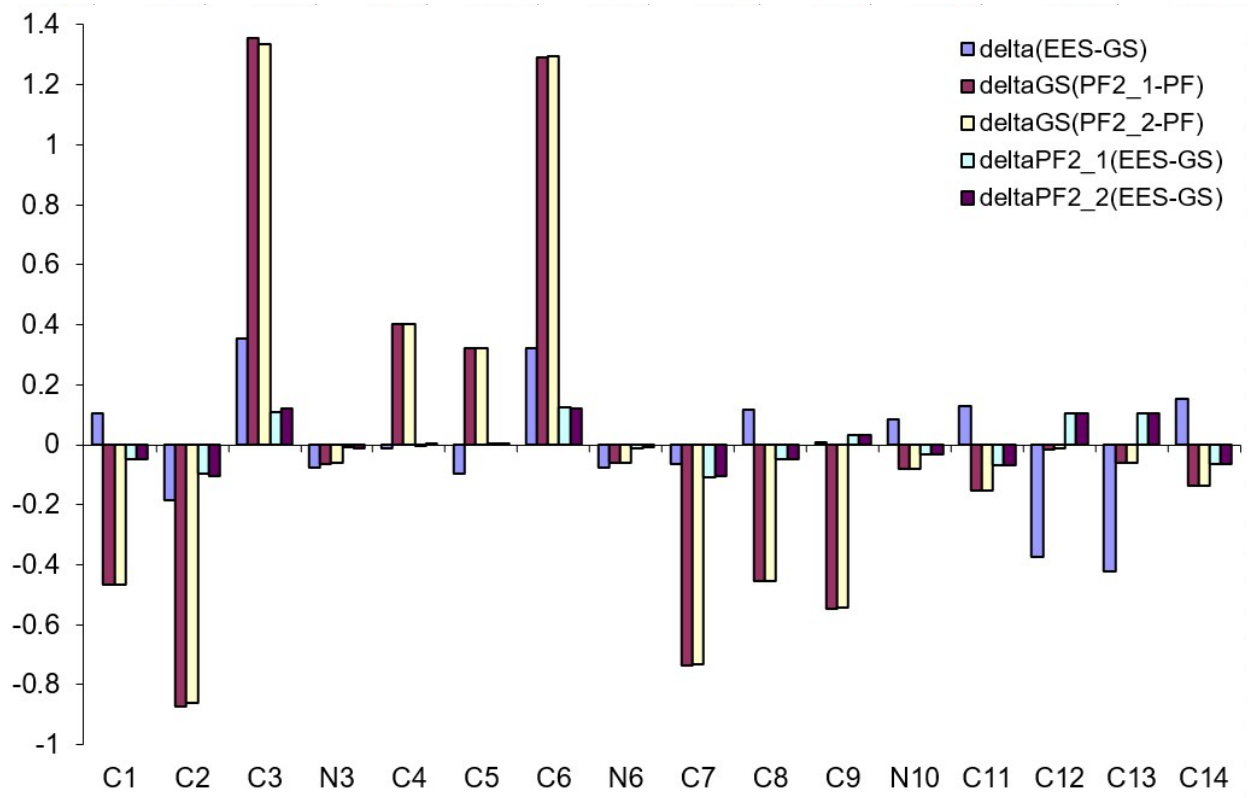

Fig. S36. Changes of NPA charges from Table S18

Table S19. NPA charges (*e*) obtained through mPW2PLYP/GD3 functional

Atom	PF GS	PF2_1 GS	deltaGS (PF2_1-PF)	PF2_2 GS	deltaGS (PF2_2-PF)
C1	-0.080	-0.525	-0.444	-0.525	-0.445
C2	0.376	-0.161	-0.537	-0.159	-0.535
C3	-0.517	0.368	0.885	0.366	0.882
N3	-0.486	-0.560	-0.074	-0.559	-0.074
C4	-0.601	-0.304	0.297	-0.304	0.297
C5	-0.555	-0.301	0.254	-0.301	0.254
C6	-0.516	0.342	0.858	0.340	0.856
N6	-0.481	-0.554	-0.074	-0.554	-0.073
C7	0.296	-0.146	-0.442	-0.145	-0.441
C8	-0.073	-0.524	-0.451	-0.524	-0.451
C9	0.424	0.117	-0.307	0.117	-0.307
N10	-0.327	-0.377	-0.050	-0.377	-0.050
C11	0.512	0.333	-0.178	0.333	-0.178
C12	-0.301	-0.120	0.181	-0.120	0.181
C13	-0.251	-0.112	0.139	-0.111	0.139
C14	0.502	0.327	-0.175	0.327	-0.175

Fig. S37. Changes of NPA charges from Table S19

Table S20. NPA charges (*e*) obtained through PBE0 functional with GD3 correction

Atom	PF			PF2_1			PF2_2			deltaGS	deltaGS
	GS	EES	delta	GS	EES	delta	GS	EES	delta	(PF2_1-PF)	(PF2_2-PF)
C1	-0.112	-0.028	0.085	-0.569	-0.564	0.004	-0.569	-0.565	0.004	-0.456	-0.457
C2	0.541	0.448	-0.092	-0.144	-0.081	0.063	-0.143	-0.079	0.063	-0.685	-0.684
C3	-0.785	-0.598	0.187	0.292	0.204	-0.089	0.290	0.200	-0.090	1.078	1.075
N3	-0.449	-0.515	-0.066	-0.525	-0.520	0.005	-0.525	-0.519	0.006	-0.077	-0.077
C4	-0.696	-0.687	0.009	-0.349	-0.349	0.001	-0.349	-0.348	0.000	0.346	0.347
C5	-0.645	-0.687	-0.041	-0.346	-0.348	-0.001	-0.346	-0.348	-0.002	0.299	0.299
C6	-0.777	-0.598	0.179	0.265	0.188	-0.076	0.262	0.185	-0.077	1.042	1.040
N6	-0.444	-0.515	-0.071	-0.520	-0.517	0.003	-0.519	-0.517	0.002	-0.076	-0.075
C7	0.451	0.448	-0.003	-0.129	-0.072	0.057	-0.128	-0.069	0.059	-0.580	-0.578
C8	-0.107	-0.028	0.079	-0.568	-0.564	0.005	-0.569	-0.563	0.005	-0.462	-0.462
C9	0.477	0.528	0.050	0.068	0.032	-0.037	0.068	0.032	-0.036	-0.409	-0.409
N10	-0.194	-0.112	0.082	-0.290	-0.255	0.036	-0.291	-0.255	0.036	-0.096	-0.096
C11	0.652	0.675	0.023	0.403	0.509	0.105	0.404	0.509	0.105	-0.248	-0.248
C12	-0.400	-0.609	-0.209	-0.203	-0.283	-0.080	-0.202	-0.283	-0.080	0.198	0.198
C13	-0.341	-0.609	-0.268	-0.194	-0.281	-0.087	-0.194	-0.280	-0.087	0.147	0.148
C14	0.641	0.675	0.034	0.398	0.506	0.108	0.398	0.505	0.107	-0.243	-0.243

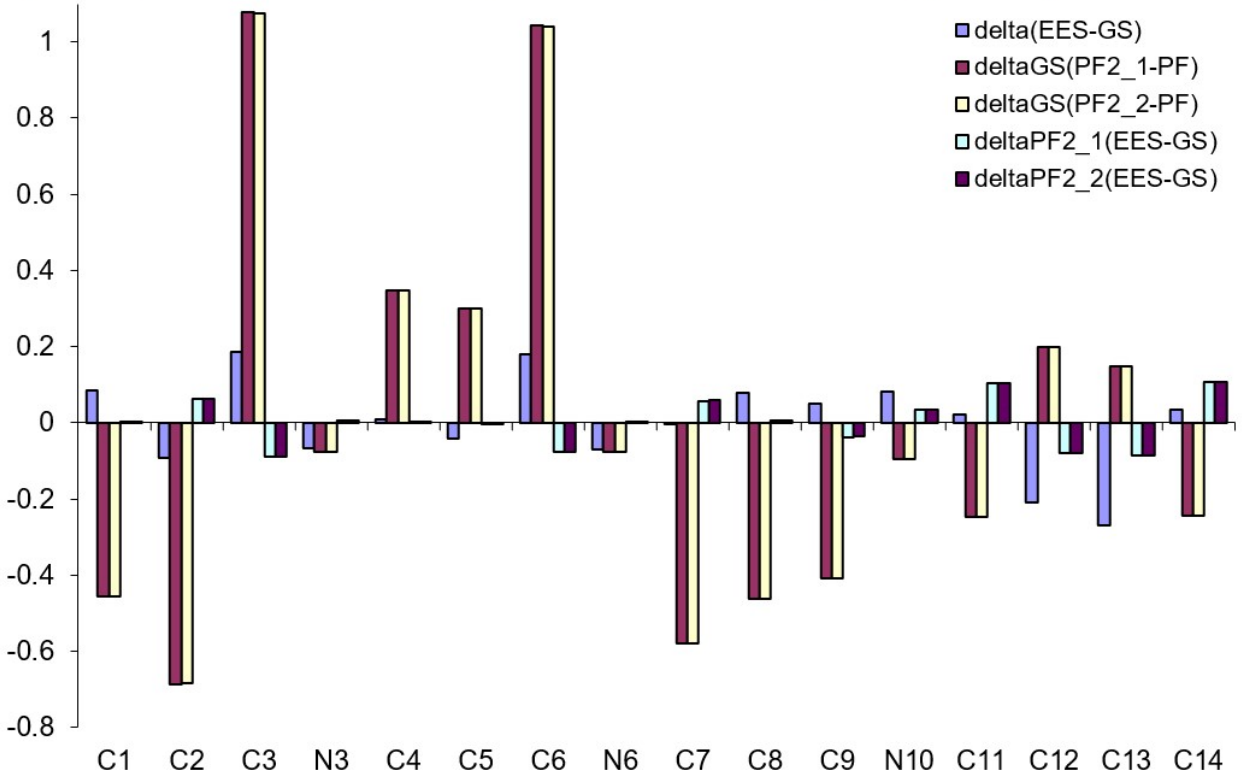

Fig. S38. Changes of NPA charges from Table S20

Table S21. NPA charges (*e*) obtained through PBE0 functional with GD3+BJ correction

Atom	PF			PF2_1			PF2_2			deltaGS	deltaGS
	GS	EES	delta	GS	EES	delta	GS	EES	delta	(PF2_1-PF)	(PF2_2-PF)
C1	-0.112	-0.028	0.084	-0.564	-0.564	0.000	-0.563	-0.563	0.000	-0.452	-0.451
C2	0.541	0.450	-0.091	-0.094	-0.094	0.000	-0.083	-0.083	0.000	-0.634	-0.624
C3	-0.785	-0.602	0.184	0.220	0.220	0.000	0.205	0.205	0.000	1.005	0.990
N3	-0.449	-0.515	-0.066	-0.523	-0.523	0.000	-0.519	-0.519	0.000	-0.074	-0.071
C4	-0.696	-0.687	0.009	-0.344	-0.344	0.000	-0.345	-0.345	0.000	0.352	0.351
C5	-0.645	-0.687	-0.041	-0.344	-0.344	0.000	-0.345	-0.345	0.000	0.301	0.301
C6	-0.777	-0.601	0.176	0.198	0.198	0.000	0.200	0.200	0.000	0.975	0.977
N6	-0.444	-0.515	-0.071	-0.518	-0.518	0.000	-0.519	-0.519	0.000	-0.075	-0.075
C7	0.451	0.449	-0.002	-0.080	-0.080	0.000	-0.079	-0.079	0.000	-0.531	-0.530
C8	-0.107	-0.029	0.078	-0.562	-0.562	0.000	-0.564	-0.564	0.000	-0.455	-0.457
C9	0.477	0.530	0.052	0.024	0.024	0.000	0.025	0.025	0.000	-0.453	-0.452
N10	-0.194	-0.112	0.082	-0.258	-0.258	0.000	-0.258	-0.258	0.000	-0.064	-0.064
C11	0.652	0.676	0.025	0.524	0.524	0.000	0.523	0.523	0.000	-0.128	-0.129
C12	-0.400	-0.609	-0.209	-0.300	-0.300	0.000	-0.298	-0.298	0.000	0.100	0.103
C13	-0.341	-0.609	-0.267	-0.297	-0.297	0.000	-0.297	-0.297	0.000	0.045	0.045
C14	0.641	0.676	0.035	0.520	0.520	0.000	0.520	0.520	0.000	-0.121	-0.121

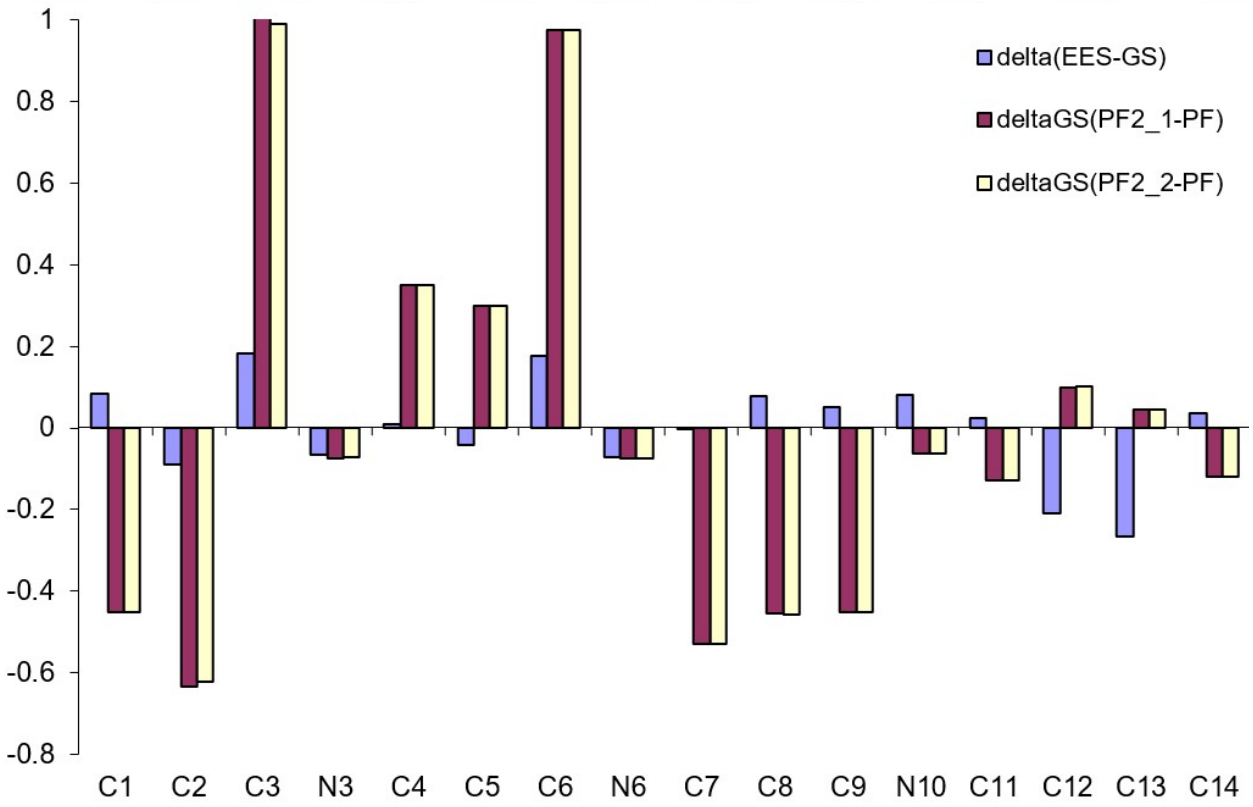

Fig. S39. Changes of NPA charges from Table S21

Table S22. NPA charges (*e*) obtained through PW6B95 functional with GD3 correction

Atom	PF			PF2_1			PF2_2			deltaGS	deltaGS
	GS	EES	delta	GS	EES	delta	GS	EES	delta	(PF2_1-PF)	(PF2_2-PF)
C1	-0.107	-0.034	0.074	-0.519	-0.526	-0.007	-0.518	-0.525	-0.007	-0.411	-0.410
C2	0.447	0.375	-0.072	-0.151	-0.142	0.009	-0.141	-0.137	0.004	-0.599	-0.588
C3	-0.590	-0.404	0.186	0.314	0.328	0.014	0.299	0.319	0.020	0.904	0.889
N3	-0.462	-0.530	-0.068	-0.523	-0.529	-0.007	-0.519	-0.528	-0.008	-0.061	-0.058
C4	-0.705	-0.715	-0.010	-0.361	-0.379	-0.017	-0.362	-0.378	-0.016	0.344	0.343
C5	-0.653	-0.715	-0.063	-0.361	-0.377	-0.015	-0.362	-0.376	-0.014	0.292	0.291
C6	-0.582	-0.403	0.178	0.290	0.314	0.023	0.292	0.314	0.022	0.872	0.874
N6	-0.458	-0.530	-0.073	-0.518	-0.527	-0.009	-0.519	-0.527	-0.008	-0.060	-0.061
C7	0.361	0.375	0.014	-0.138	-0.135	0.003	-0.137	-0.134	0.003	-0.499	-0.498
C8	-0.102	-0.034	0.067	-0.516	-0.524	-0.007	-0.518	-0.525	-0.007	-0.415	-0.416
C9	0.491	0.561	0.070	0.124	0.135	0.011	0.126	0.135	0.010	-0.367	-0.365
N10	-0.224	-0.149	0.075	-0.277	-0.278	-0.001	-0.277	-0.278	-0.001	-0.053	-0.053
C11	0.612	0.646	0.035	0.518	0.465	-0.053	0.518	0.464	-0.054	-0.094	-0.094
C12	-0.363	-0.568	-0.205	-0.305	-0.246	0.060	-0.303	-0.243	0.060	0.058	0.060
C13	-0.311	-0.568	-0.257	-0.302	-0.243	0.059	-0.302	-0.243	0.059	0.009	0.009
C14	0.601	0.646	0.045	0.516	0.463	-0.053	0.515	0.463	-0.053	-0.085	-0.086

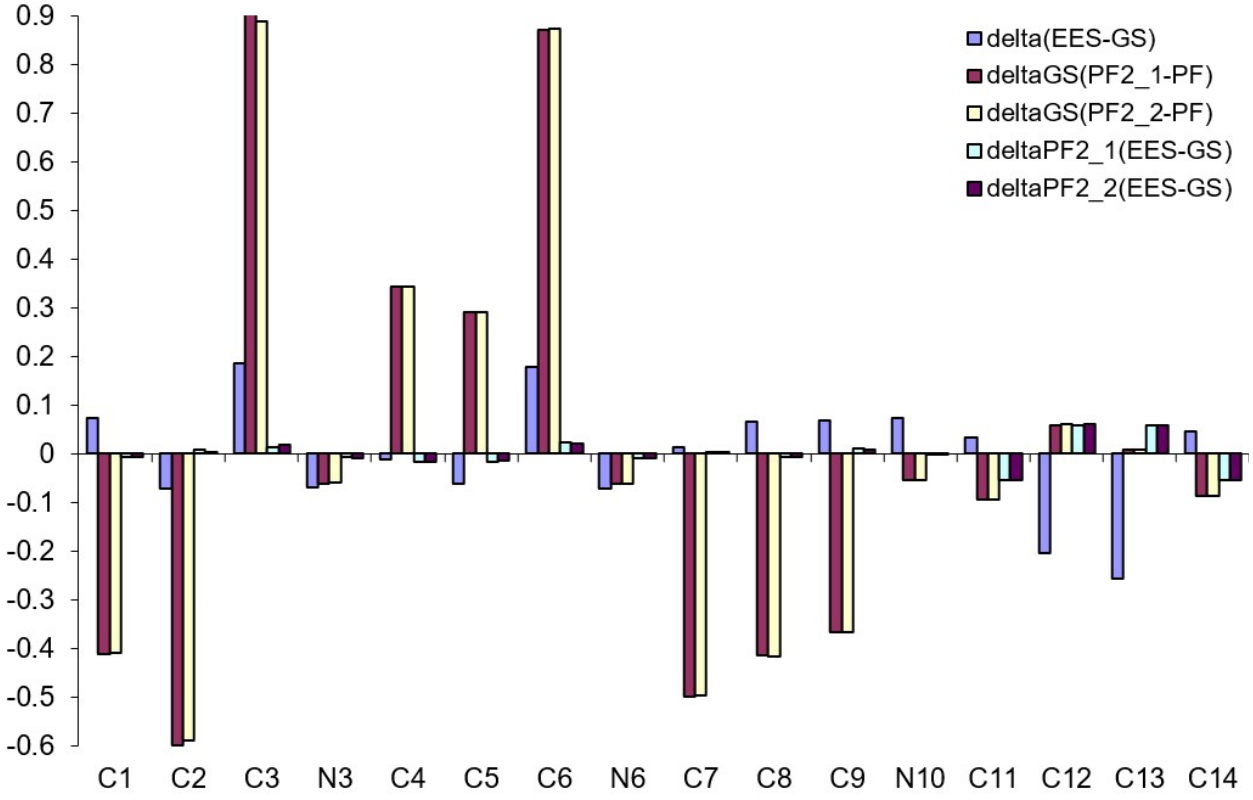

Fig. S40. Changes of NPA charges from Table S22

Table S23. NPA charges (*e*) obtained through PW6B95 functional with GD3+BJ correction

Atom	PF			PF2_1			PF2_2			deltaGS	deltaGS
	GS	EES	delta	GS	EES	delta	GS	EES	delta	(PF2_1-PF)	(PF2_2-PF)
C1	-0.107	-0.034	0.073	-0.489	-0.563	-0.074	-0.487	-0.563	-0.076	-0.381	-0.380
C2	0.447	0.376	-0.071	-0.088	-0.213	-0.125	-0.101	-0.211	-0.109	-0.535	-0.548
C3	-0.590	-0.406	0.184	0.201	0.406	0.205	0.223	0.404	0.182	0.791	0.813
N3	-0.462	-0.530	-0.068	-0.492	-0.528	-0.036	-0.497	-0.528	-0.031	-0.031	-0.035
C4	-0.705	-0.715	-0.010	-0.389	-0.394	-0.005	-0.388	-0.394	-0.005	0.316	0.317
C5	-0.653	-0.715	-0.062	-0.388	-0.393	-0.006	-0.387	-0.393	-0.007	0.265	0.266
C6	-0.582	-0.405	0.176	0.208	0.401	0.193	0.214	0.396	0.182	0.790	0.795
N6	-0.458	-0.530	-0.072	-0.494	-0.527	-0.033	-0.495	-0.526	-0.031	-0.036	-0.037
C7	0.361	0.375	0.015	-0.091	-0.209	-0.118	-0.098	-0.206	-0.108	-0.452	-0.459
C8	-0.102	-0.034	0.067	-0.488	-0.563	-0.075	-0.486	-0.563	-0.077	-0.387	-0.385
C9	0.491	0.562	0.070	0.202	0.217	0.015	0.200	0.218	0.018	-0.289	-0.291
N10	-0.224	-0.149	0.075	-0.279	-0.314	-0.035	-0.279	-0.313	-0.034	-0.055	-0.055
C11	0.612	0.647	0.036	0.548	0.450	-0.098	0.546	0.450	-0.097	-0.064	-0.065
C12	-0.363	-0.568	-0.205	-0.355	-0.211	0.144	-0.358	-0.211	0.147	0.008	0.005
C13	-0.311	-0.568	-0.257	-0.356	-0.209	0.147	-0.356	-0.209	0.146	-0.045	-0.045
C14	0.601	0.647	0.046	0.546	0.449	-0.097	0.546	0.450	-0.096	-0.054	-0.055

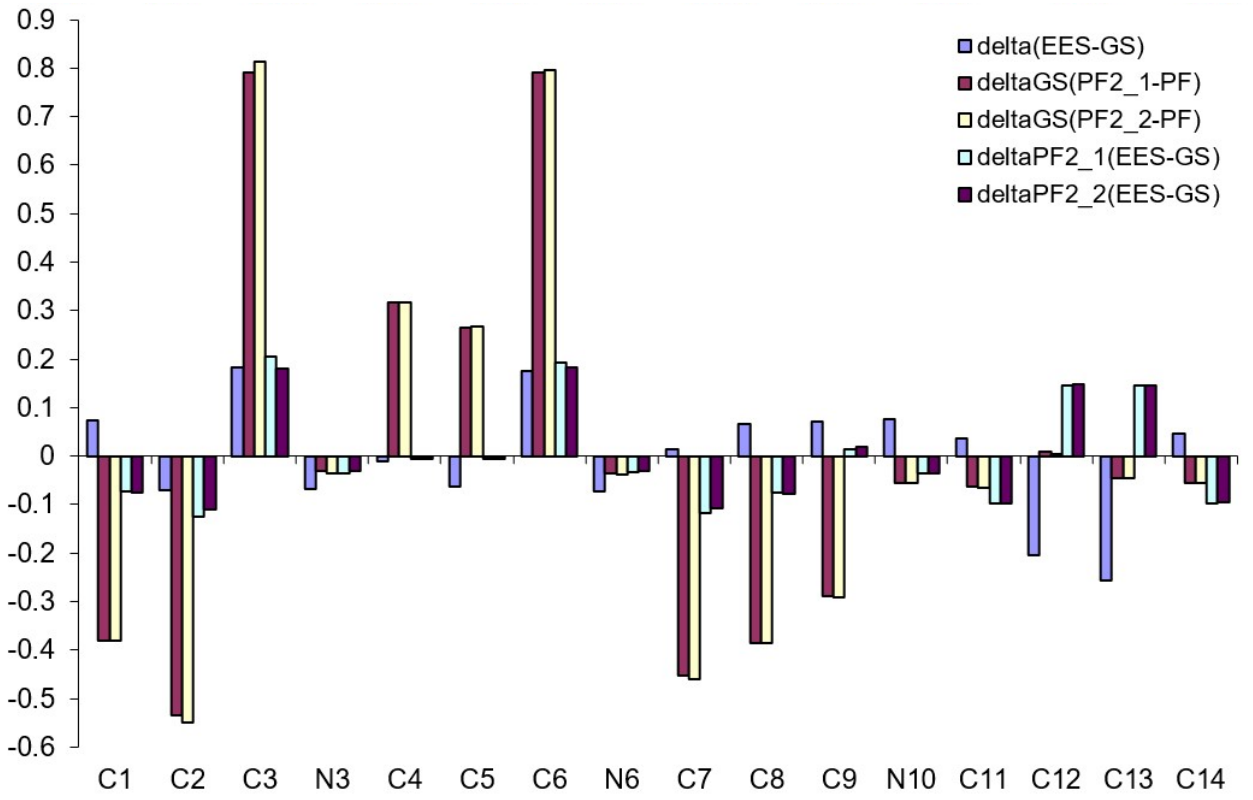

Fig. S41. Changes of NPA charges from Table S23

Table S24. NPA charges (*e*) obtained through ωB97XD functional

Atom	PF			PF2_1			PF2_2			deltaGS	deltaGS
	GS	EES	delta	GS	EES	delta	GS	EES	delta	(PF2_1-PF)	(PF2_2-PF)
C1	-0.018	-0.017	0.001	-0.438	-0.350	0.088	-0.438	-0.350	0.088	-0.420	-0.420
C2	0.355	0.350	-0.005	-0.094	-0.063	0.031	-0.099	-0.063	0.036	-0.450	-0.455
C3	-0.407	-0.385	0.022	0.202	0.074	-0.128	0.209	0.074	-0.135	0.609	0.616
N3	-0.550	-0.565	-0.015	-0.529	-0.507	0.022	-0.530	-0.507	0.023	0.021	0.020
C4	-0.590	-0.594	-0.005	-0.275	-0.242	0.033	-0.275	-0.242	0.033	0.315	0.314
C5	-0.588	-0.594	-0.006	-0.273	-0.278	-0.005	-0.273	-0.278	-0.005	0.316	0.315
C6	-0.410	-0.385	0.025	0.188	0.283	0.095	0.196	0.284	0.088	0.598	0.606
N6	-0.548	-0.565	-0.017	-0.526	-0.523	0.004	-0.528	-0.523	0.005	0.022	0.020
C7	0.356	0.350	-0.006	-0.088	-0.013	0.075	-0.094	-0.014	0.080	-0.445	-0.450
C8	-0.018	-0.017	0.001	-0.439	-0.400	0.038	-0.439	-0.400	0.039	-0.421	-0.422
C9	0.414	0.413	-0.001	0.016	-0.054	-0.070	0.015	-0.054	-0.070	-0.398	-0.398
N10	-0.194	-0.194	-0.001	-0.323	-0.314	0.010	-0.323	-0.314	0.009	-0.130	-0.129
C11	0.525	0.521	-0.004	0.290	0.163	-0.127	0.291	0.163	-0.128	-0.235	-0.234
C12	-0.470	-0.468	0.002	-0.120	-0.043	0.077	-0.122	-0.043	0.079	0.349	0.348
C13	-0.470	-0.468	0.002	-0.116	-0.248	-0.132	-0.117	-0.248	-0.131	0.354	0.353
C14	0.525	0.521	-0.004	0.289	0.268	-0.021	0.290	0.268	-0.022	-0.236	-0.235

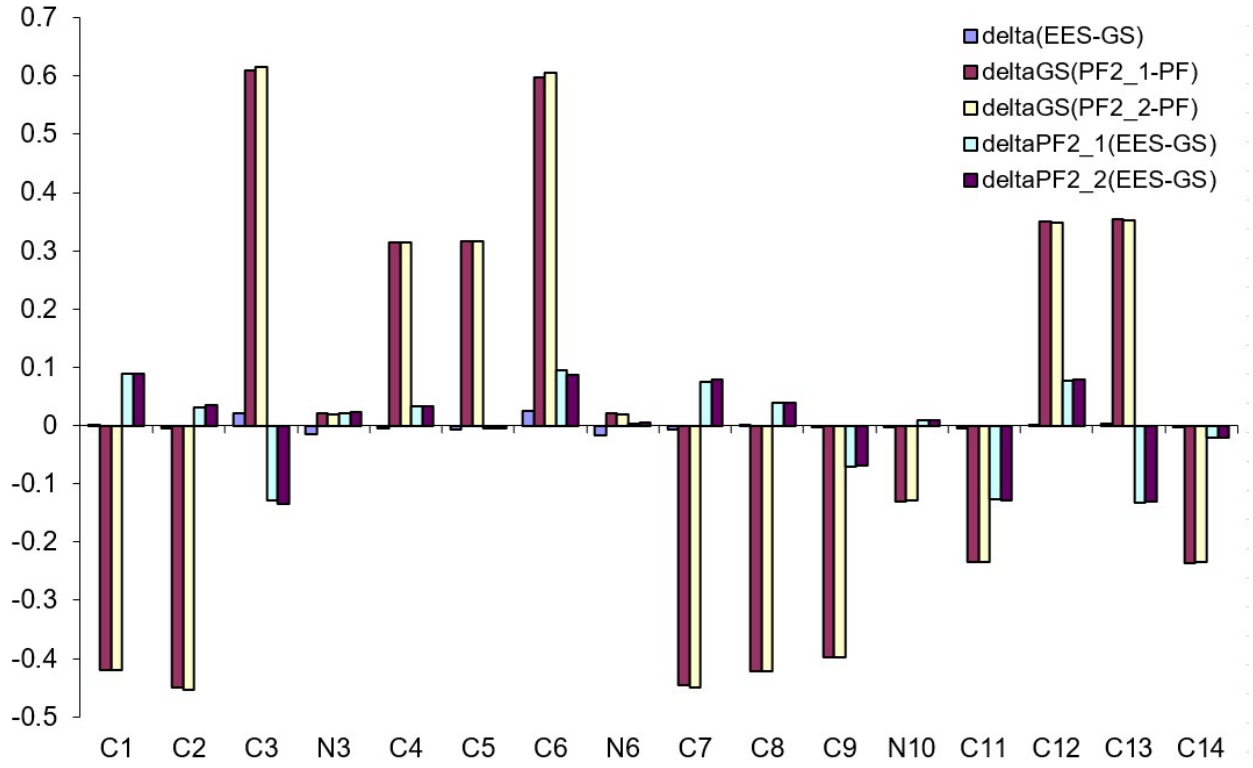

Fig. S42. Changes of NPA charges from Table S24

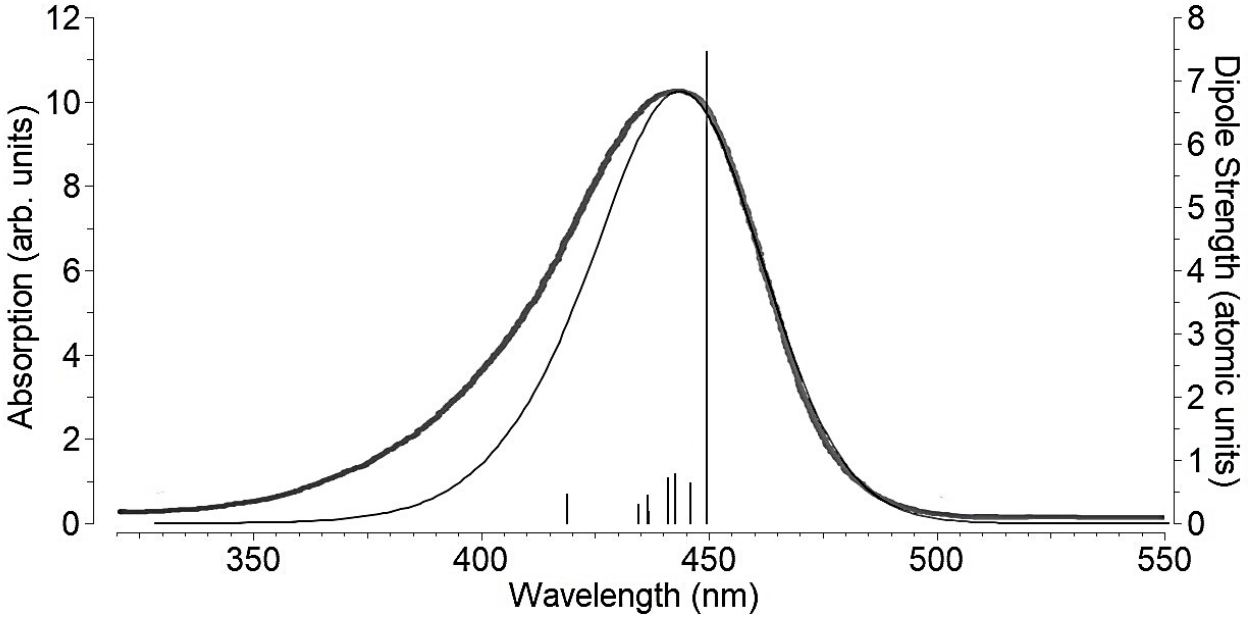

Fig. S43. Calculated (thin line, APFD functional) and experimental (thick line, adapted from Ref. [71], permission 5453060925345 from Wiley) absorption spectra of PF monomer in aqueous solution

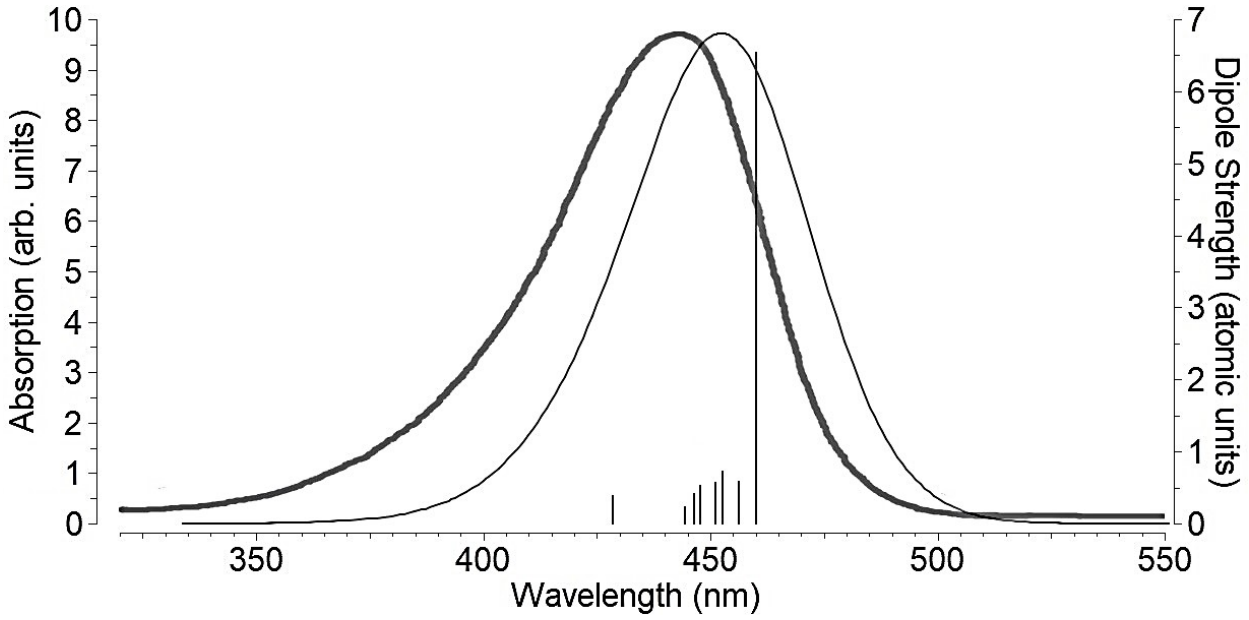

Fig. S44. Calculated (thin line, B3LYP functional with GD2 correction) and experimental (thick line [71]) absorption spectra of PF monomer in aqueous solution

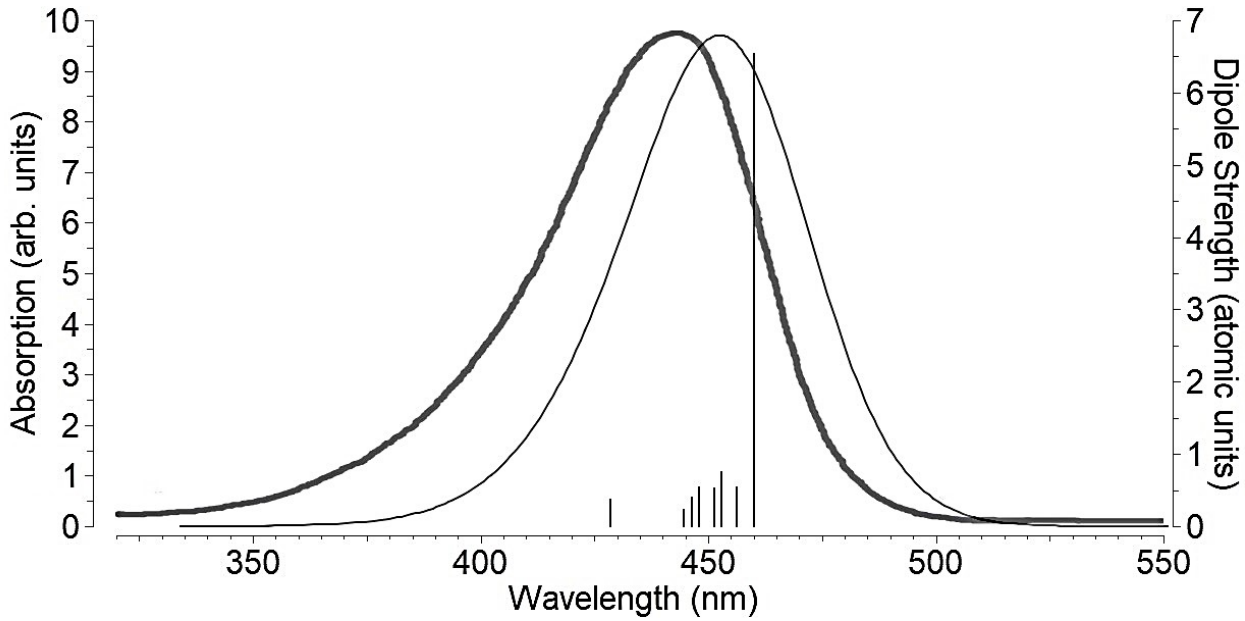

Fig. S45. Calculated (thin line, B3LYP functional with GD3 correction) and experimental (thick line [71]) absorption spectra of PF monomer in aqueous solution

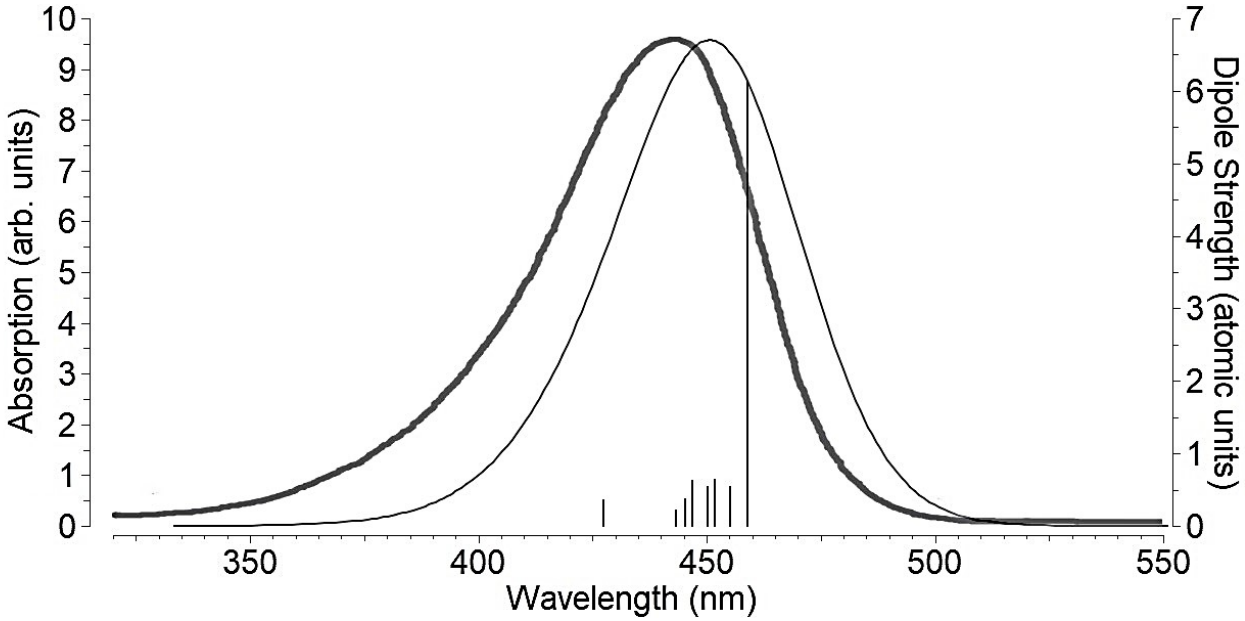

Fig. S46. Calculated (thin line, B3LYP functional with GD3+BJ correction) and experimental (thick line [71]) absorption spectra of PF monomer in aqueous solution

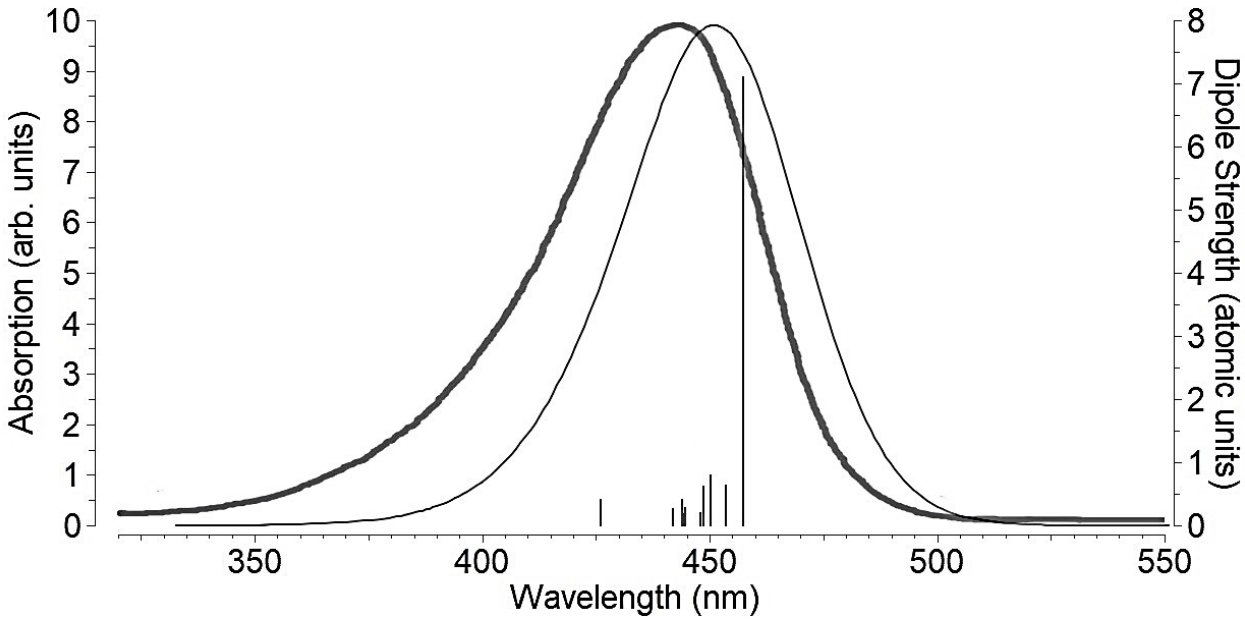

Fig. S47. Calculated (thin line, B3PW91 functional with GD3 correction) and experimental (thick line [71]) absorption spectra of PF monomer in aqueous solution

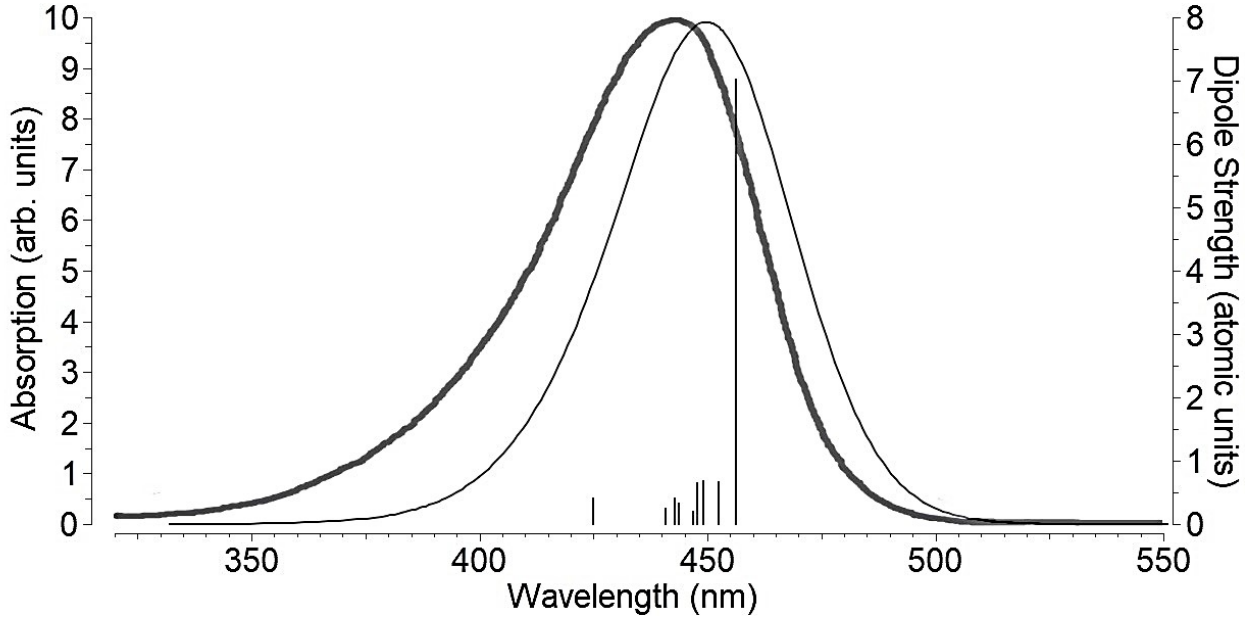

Fig. S48. Calculated (thin line, B3PW91 functional with GD3+BJ correction) and experimental (thick line [71]) absorption spectra of PF monomer in aqueous solution

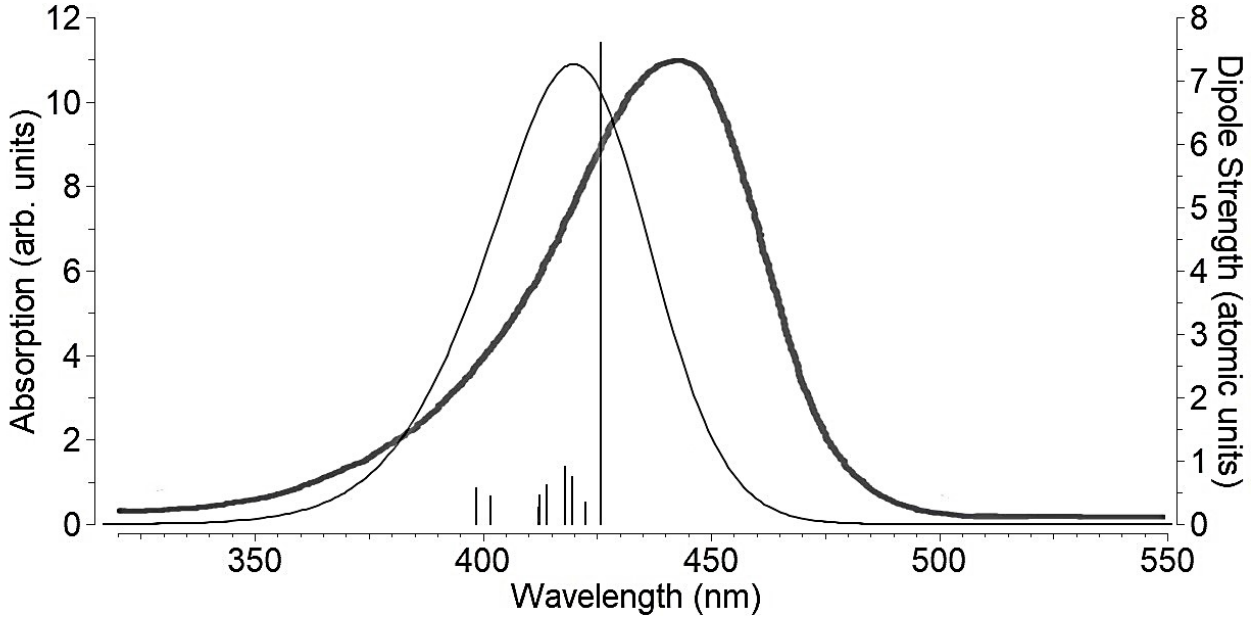

Fig. S49. Calculated (thin line, BMK functional with GD3 correction) and experimental (thick line [71]) absorption spectra of PF monomer in aqueous solution

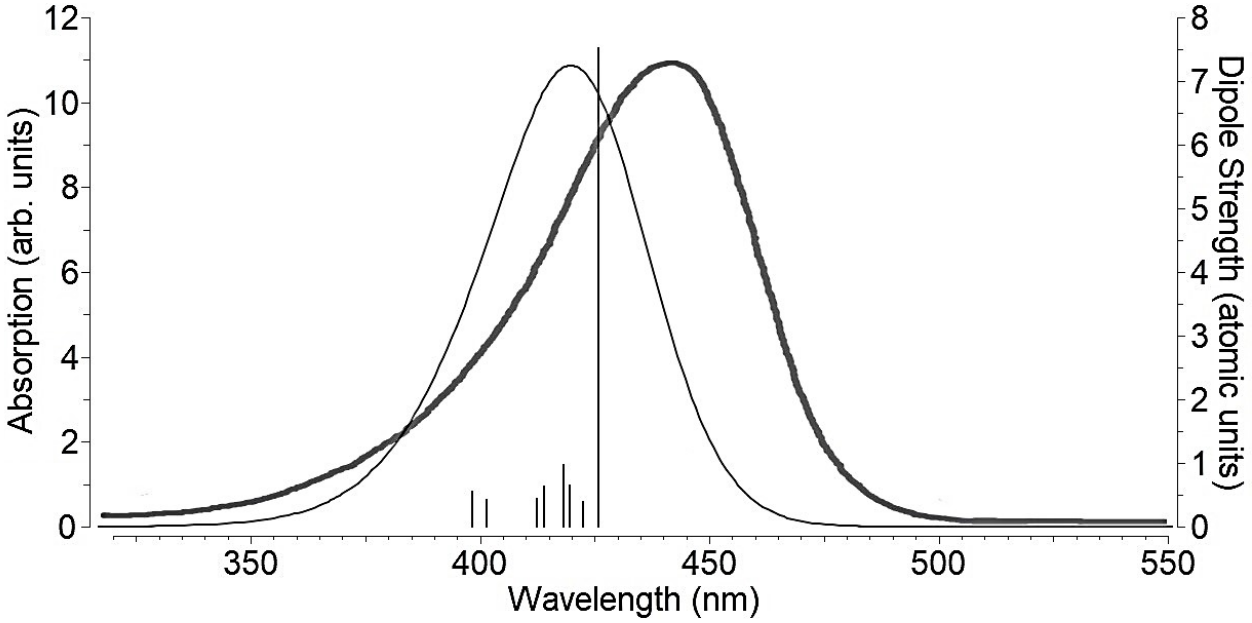

Fig. S50. Calculated (thin line, BMK functional with GD3+BJ correction) and experimental (thick line [71]) absorption spectra of PF monomer in aqueous solution

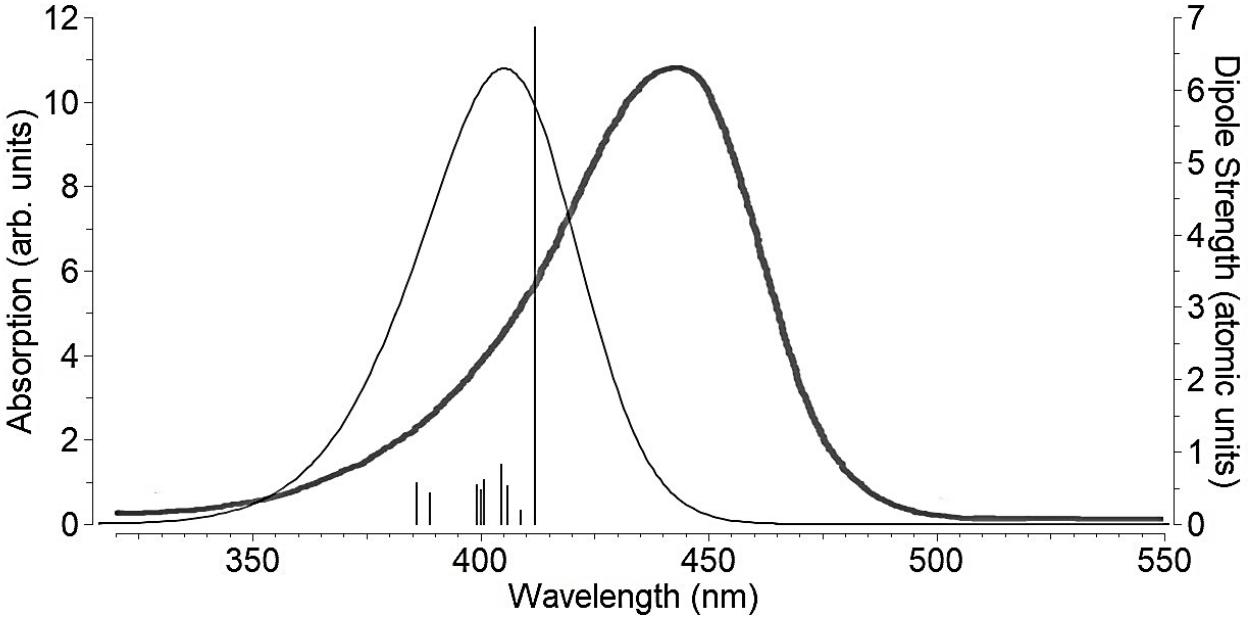

Fig. S51. Calculated (thin line, CAM-B3LYP functional with GD3 correction) and experimental (thick line [71]) absorption spectra of PF monomer in aqueous solution

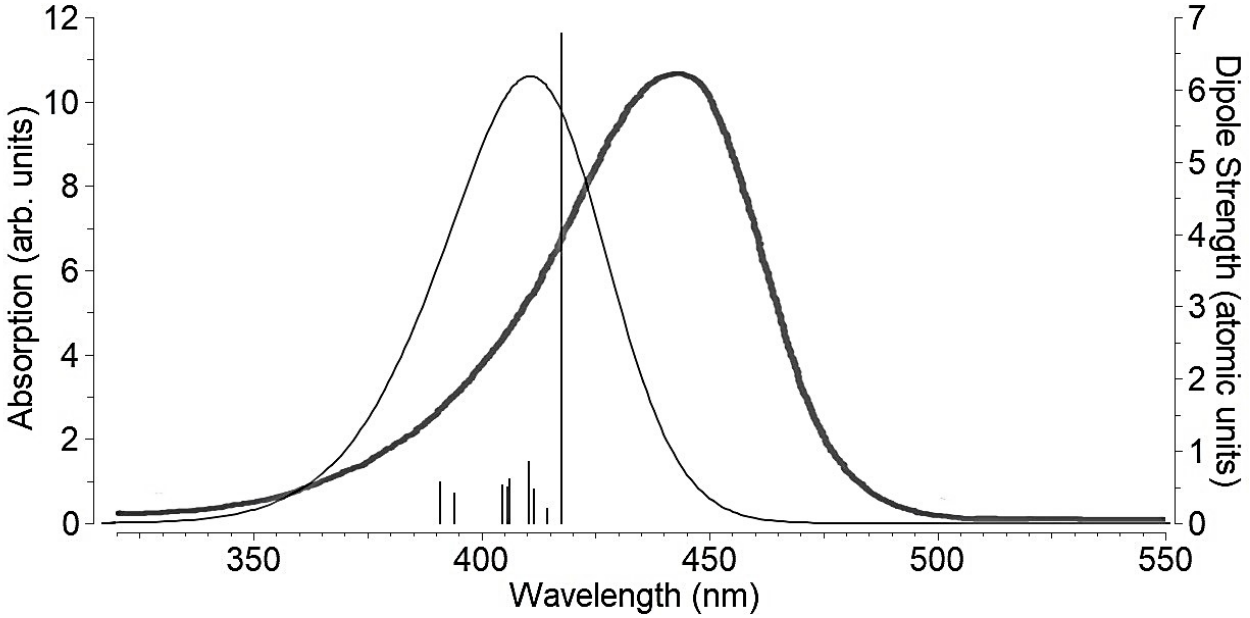

Fig. S52. Calculated (thin line, CAM-B3LYP functional with GD3+BJ correction) and experimental (thick line [71]) absorption spectra of PF monomer in aqueous solution

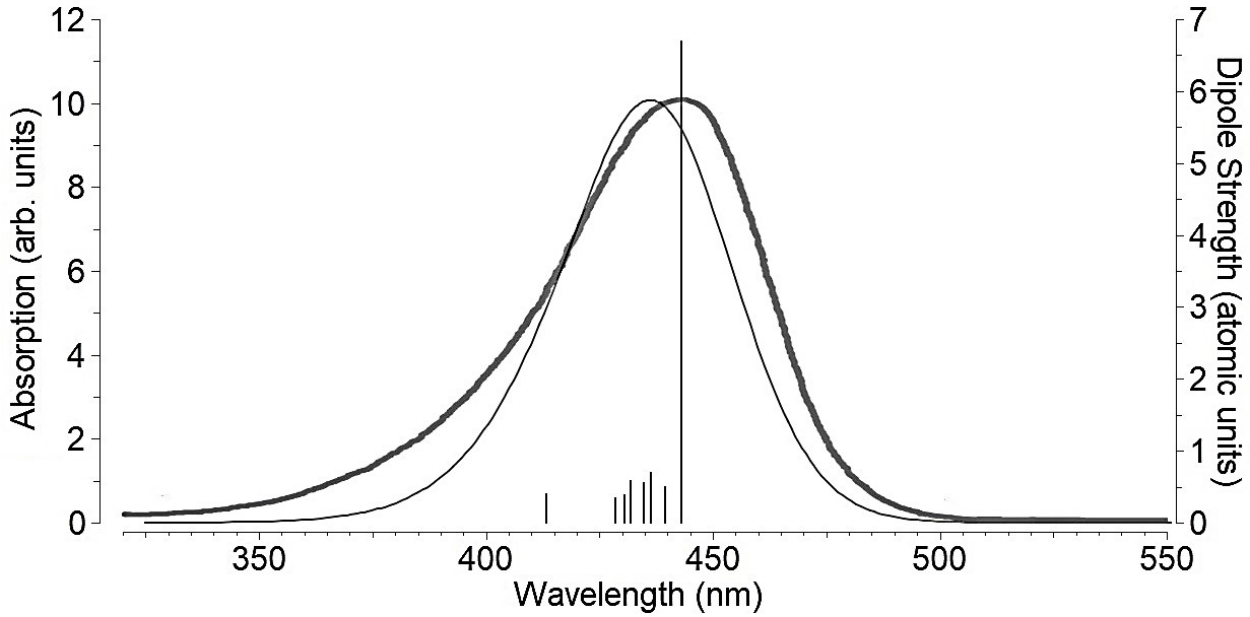

Fig. S53. Calculated (thin line, M05 functional with GD3 correction) and experimental (thick line [71]) absorption spectra of PF monomer in aqueous solution

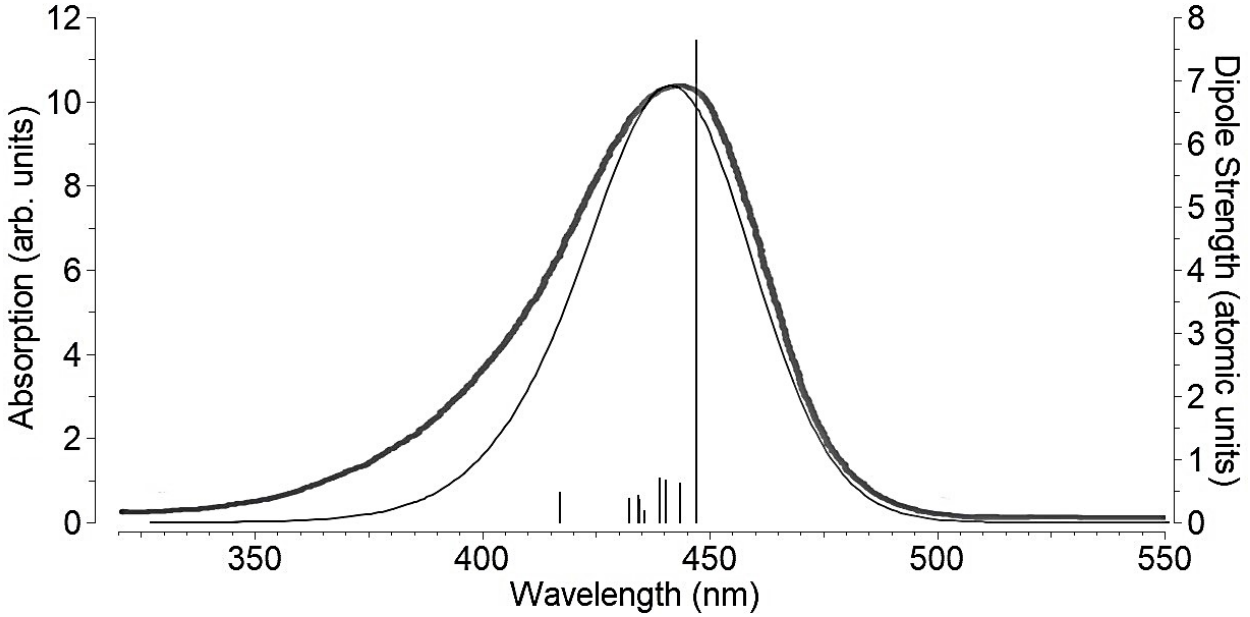

Fig. S54. Calculated (thin line, M06 functional) and experimental (thick line [71]) absorption spectra of PF monomer in aqueous solution

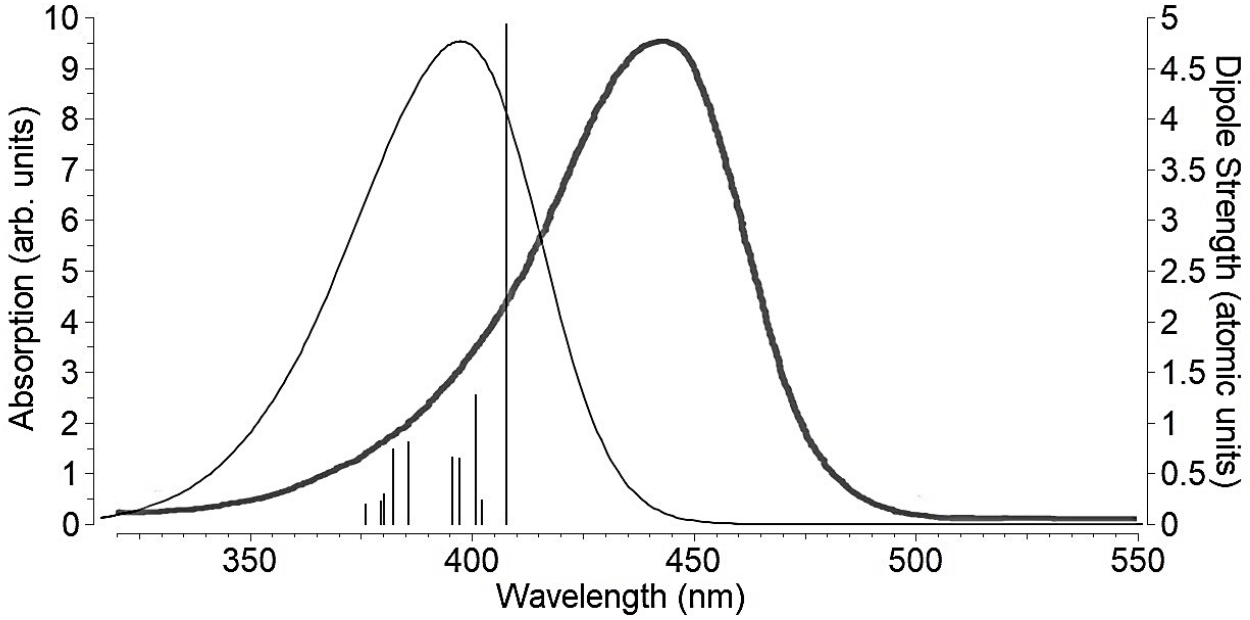

Fig. S55. Calculated (thin line, M06HF functional) and experimental (thick line [71]) absorption spectra of PF monomer in aqueous solution

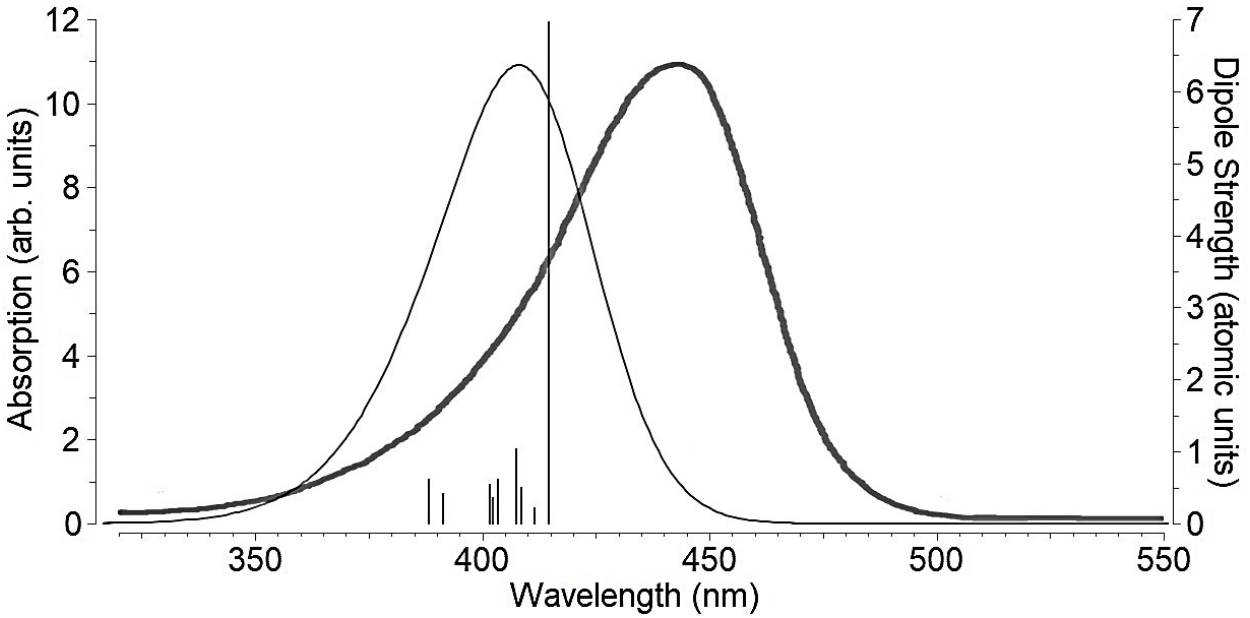

Fig. S56. Calculated (thin line, M052X functional) and experimental (thick line [71]) absorption spectra of PF monomer in aqueous solution

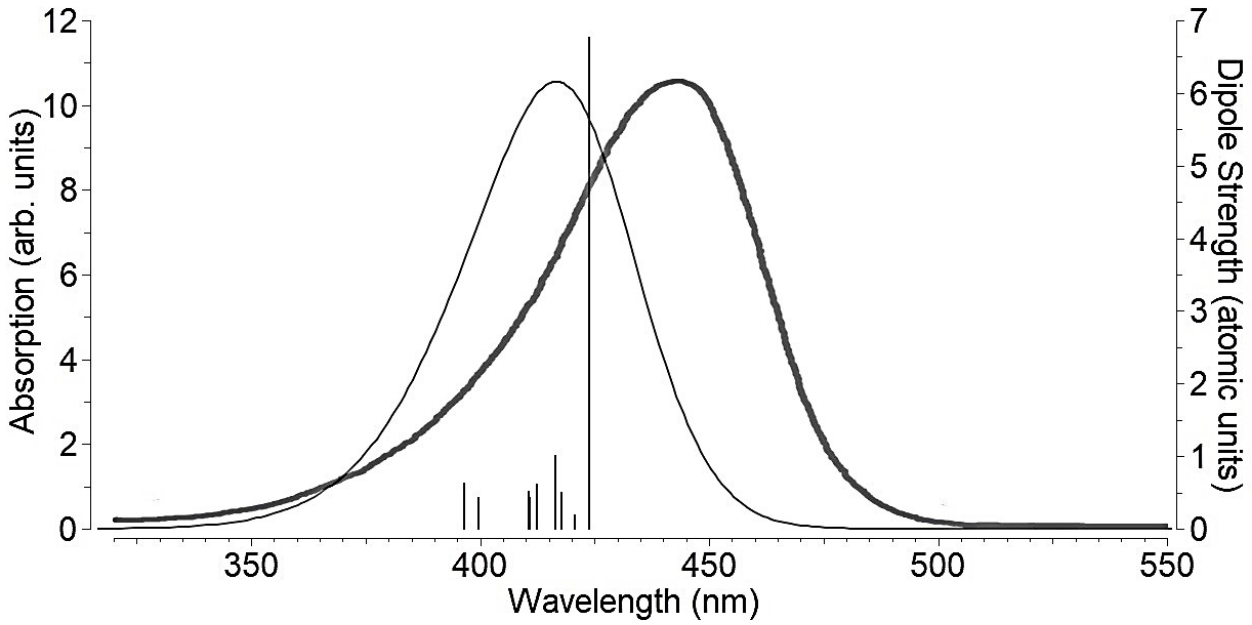

Fig. S57. Calculated (thin line, M062X functional) and experimental (thick line [71]) absorption spectra of PF monomer in aqueous solution

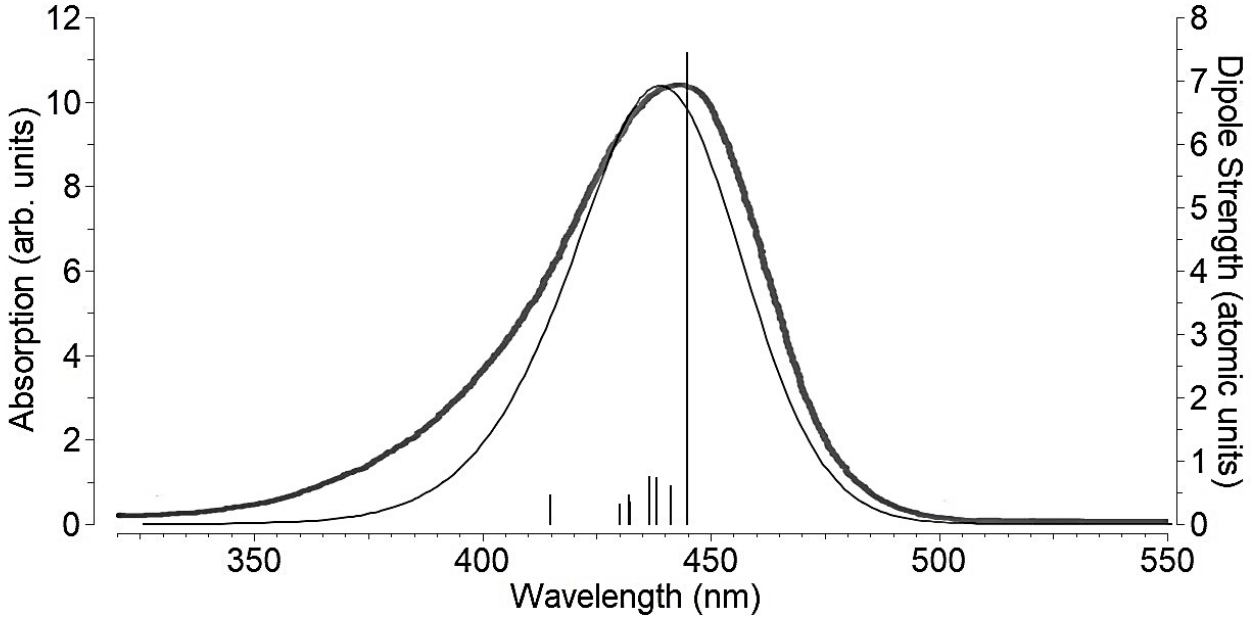

Fig. S58. Calculated (thin line, PBE0 functional with GD3 correction) and experimental (thick line [71]) absorption spectra of PF monomer in aqueous solution

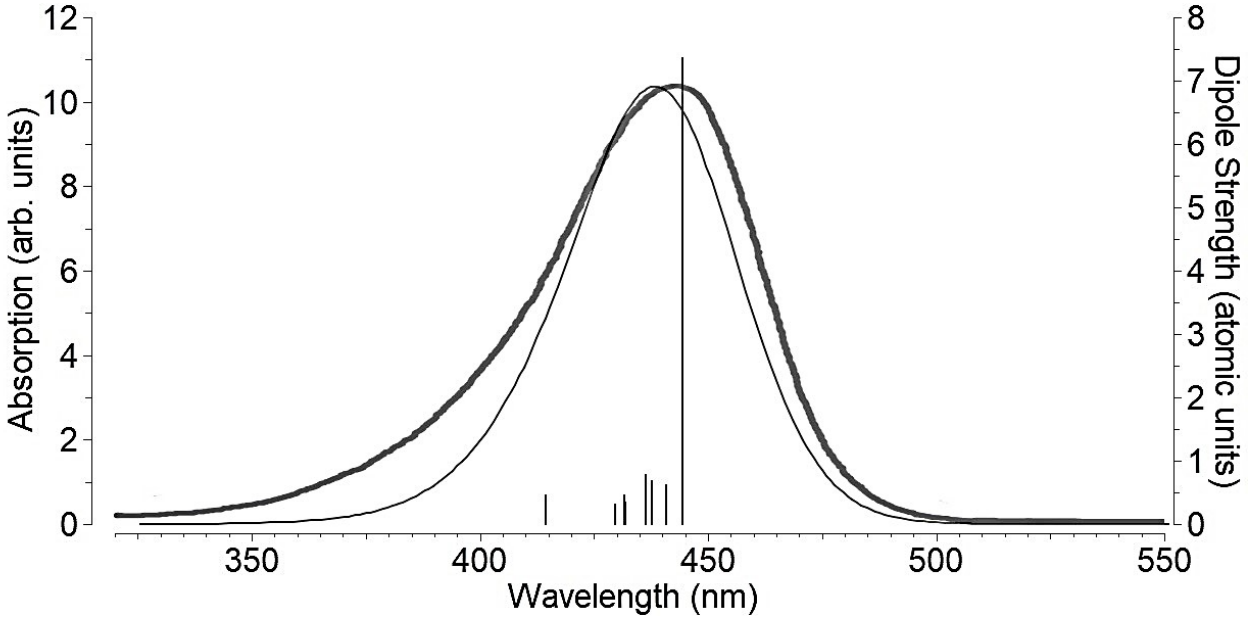

Fig. S59. Calculated (thin line, PBE0 functional with GD3+BJ correction) and experimental (thick line [71]) absorption spectra of PF monomer in aqueous solution

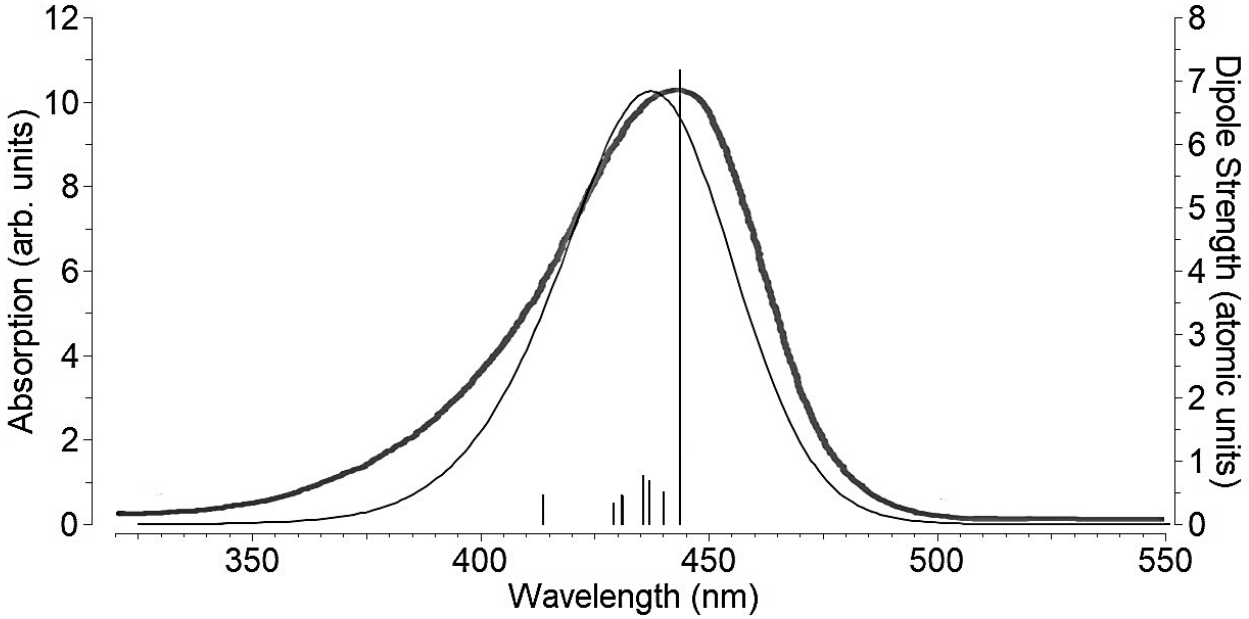

Fig. S60. Calculated (thin line, PW6B95 functional with GD3 correction) and experimental (thick line [71]) absorption spectra of PF monomer in aqueous solution

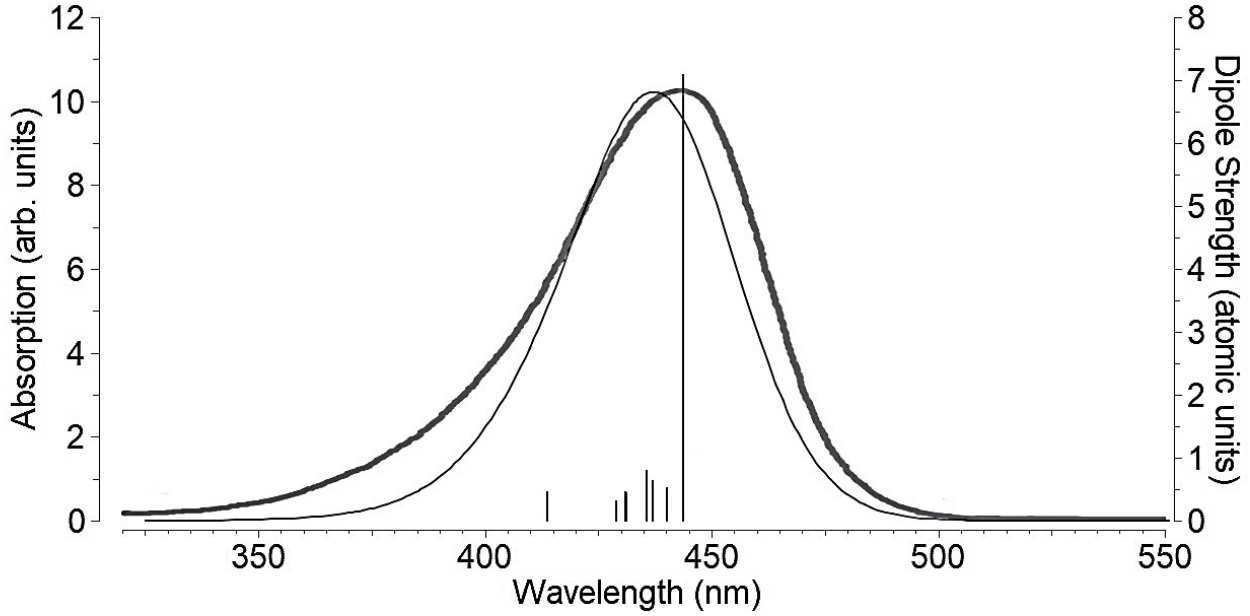

Fig. S61. Calculated (thin line, PW6B95 functional with GD3+BJ correction) and experimental (thick line [71]) absorption spectra of PF monomer in aqueous solution

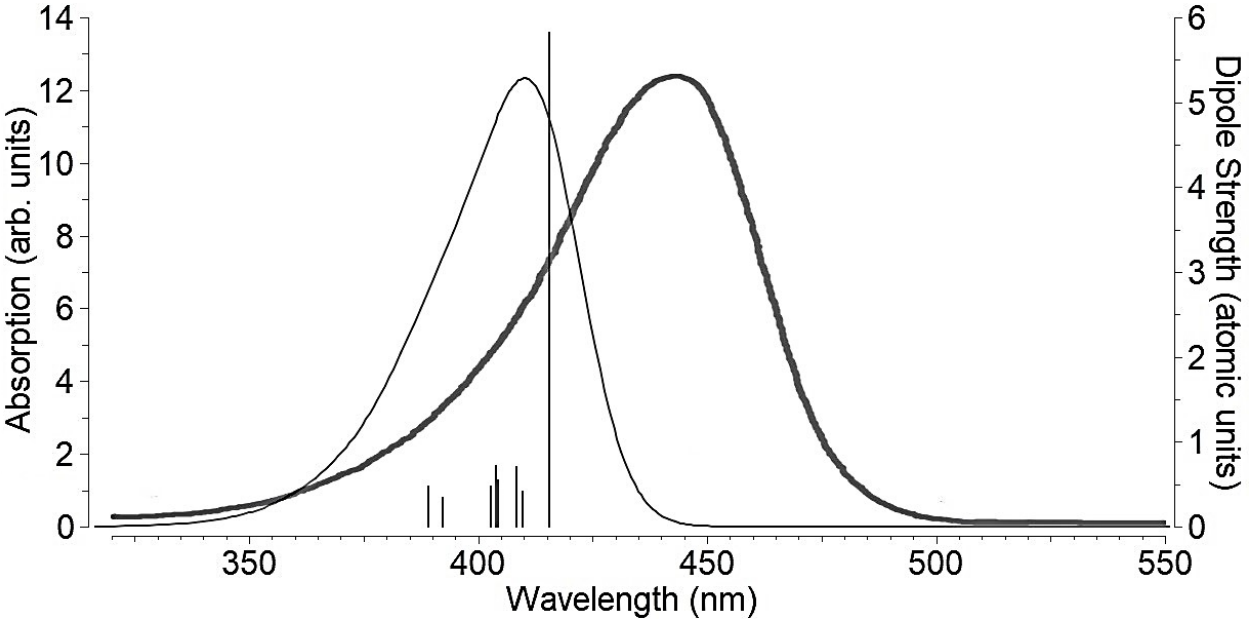

Fig. S62. Calculated (thin line, ωB97XD functional) and experimental (thick line [71]) absorption spectra of PF monomer in aqueous solution

Table S25. Parameters of 0→0 transition in PF dimer (M062X functional)

Transition	λ (nm)	ν (cm^{-1})	I	p (a.u.)
$0_0 \rightarrow 0^0$	416	-	64.0	0.00727

Table S26. Vibronic transitions in PF dimer (M06HF functional)

#	Transition	λ (nm)	ν (cm^{-1})	I	p (a.u.)
1	$0_0 \rightarrow 0^0$	392.4	-	37610	4.02
2	$0_0 \rightarrow 1^1$	392.1	20.3	9576	1.02
3	$0_0 \rightarrow 4^1$	391.3	72.3	37890	4.04
4	$0_0 \rightarrow 1^1 4^1$	391.0	20.3+72.3	9288	0.989
5	$0_0 \rightarrow 7^1$	390.9	98.9	4863	0.518
6	$0_0 \rightarrow 4^1$	390.2	145	15840	1.68
7	$0_0 \rightarrow 1^1 4^2$	389.9	20.3+145	3707	0.394
8	$0_0 \rightarrow 4^1 7^1$	389.8	72.3+98.9	3742	0.397
9	$0_0 \rightarrow 4^3$	389.1	217	3442	0.365
10	$0_0 \rightarrow 29^1$	386.0	419	4058	0.427
11	$0_0 \rightarrow 4^1 29^1$	385.0	72.3+419	3923	0.411

Table S27. Vibronic transitions in PF dimer (ωB97XD functional)

#	Transition	λ (nm)	ν (cm^{-1})	I	p (a.u.)
1	$0_0 \rightarrow 0^0$	409.0	-	140.2	0.0156
2	$0_0 \rightarrow 2^3$	407.6	79.9	5500	0.611
3	$0_0 \rightarrow 2^4$	407.2	107	7715	0.856
4	$0_0 \rightarrow 2^5$	406.8	133	8203	0.909
5	$0_0 \rightarrow 2^3 3^1$	406.7	79.9+59.1	5392	0.597
6	$0_0 \rightarrow 2^6$	406.3	160	6853	0.759
7	$0_0 \rightarrow 2^4 3^1$	406.2	107+58	7560	0.837
8	$0_0 \rightarrow 2^7$	405.9	186	4600	0.509
9	$0_0 \rightarrow 2^5 3^1$	405.8	133+59.1	8034	0.888
10	$0_0 \rightarrow 2^6 3^1$	405.3	160+59.1	6708	0.741
11	$0_0 \rightarrow 2^4 3^2$	405.3	107+117	3539	0.391
12	$0_0 \rightarrow 2^7 3^1$	404.9	186+59.1	4500	0.496
13	$0_0 \rightarrow 2^5 3^2$	404.8	133+117	3758	0.415
14	$0_0 \rightarrow 2^6 3^2$	404.4	160+117	3136	0.346

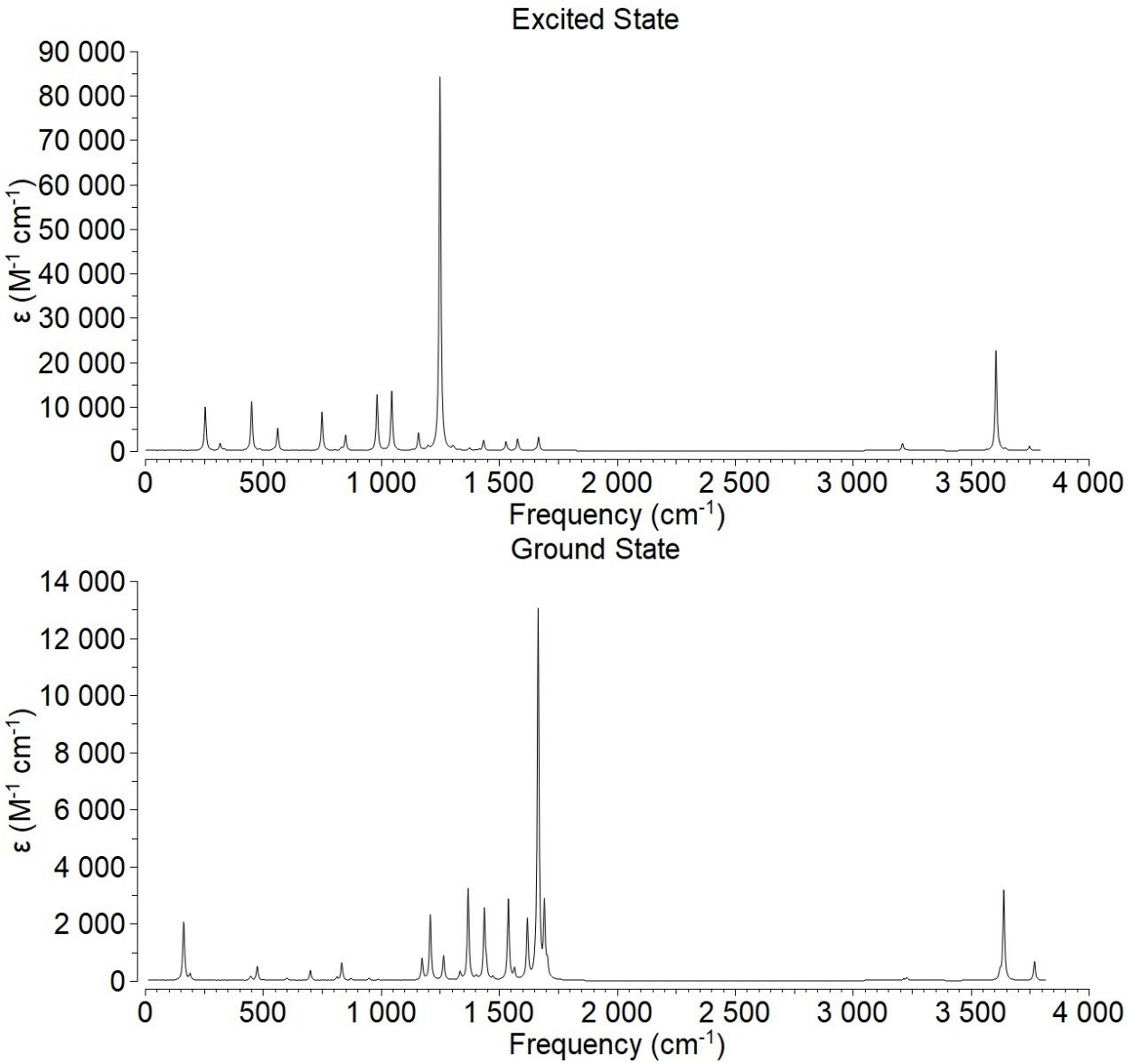

Fig. S63. Calculated vibrational spectra of PF monomer (APFD functional)

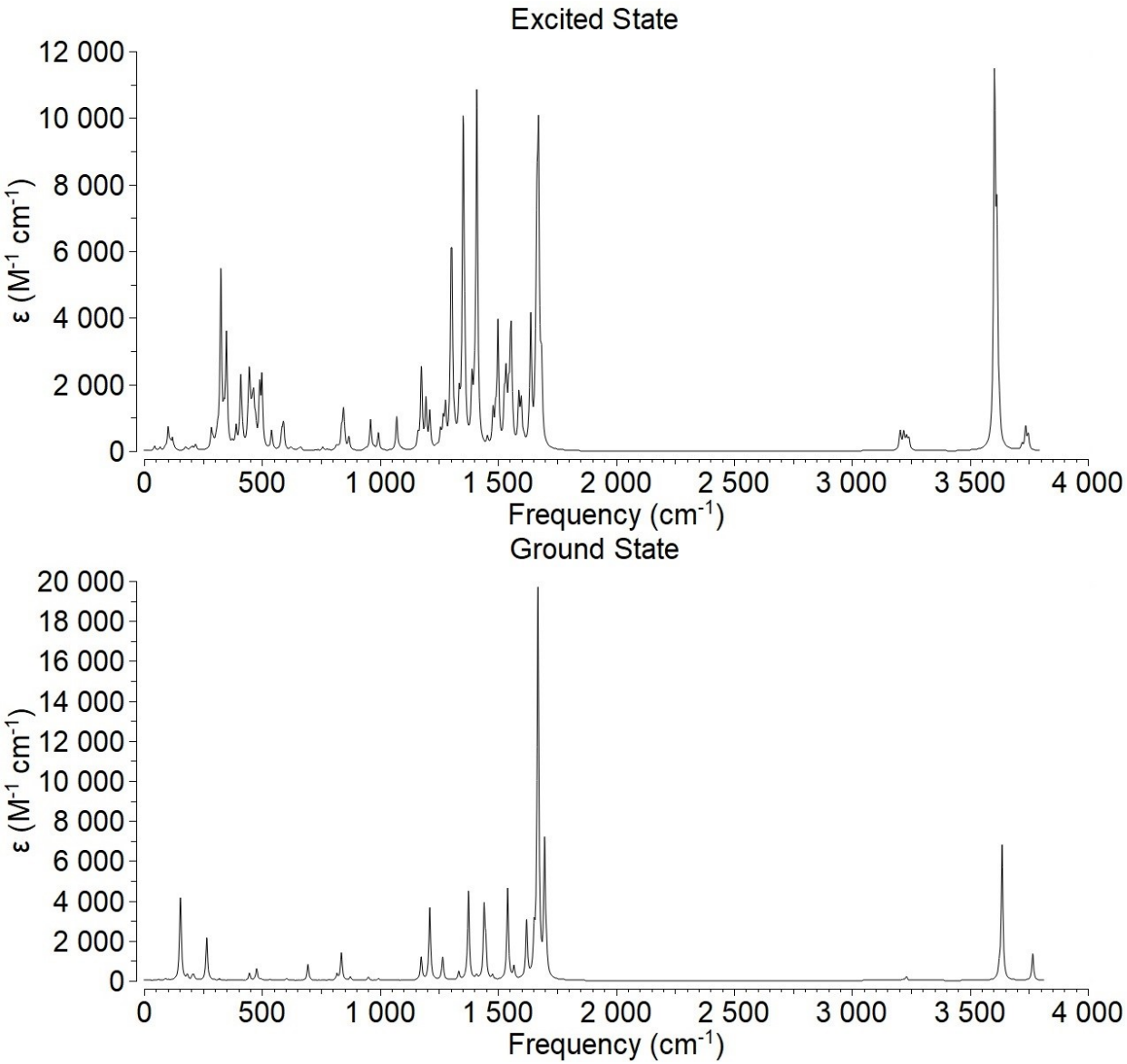

Fig. S64. Calculated vibrational spectra of PF dimer (APFD functional)

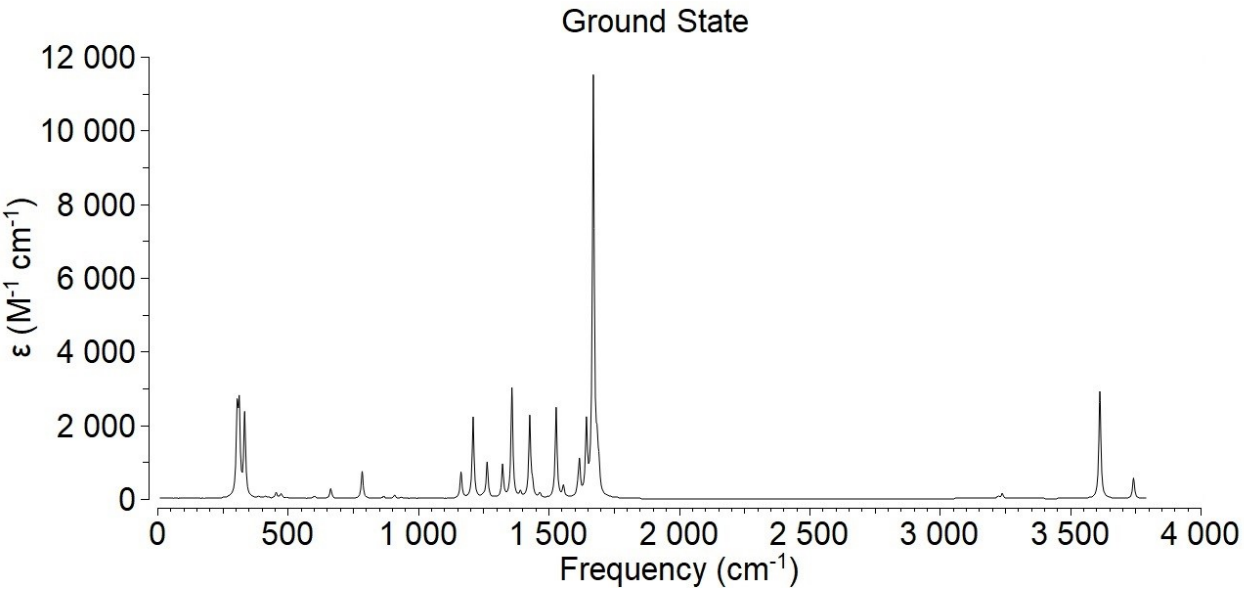

Fig. S65. Calculated vibrational spectra of PF monomer (B2PLYP functional with GD2 correction)

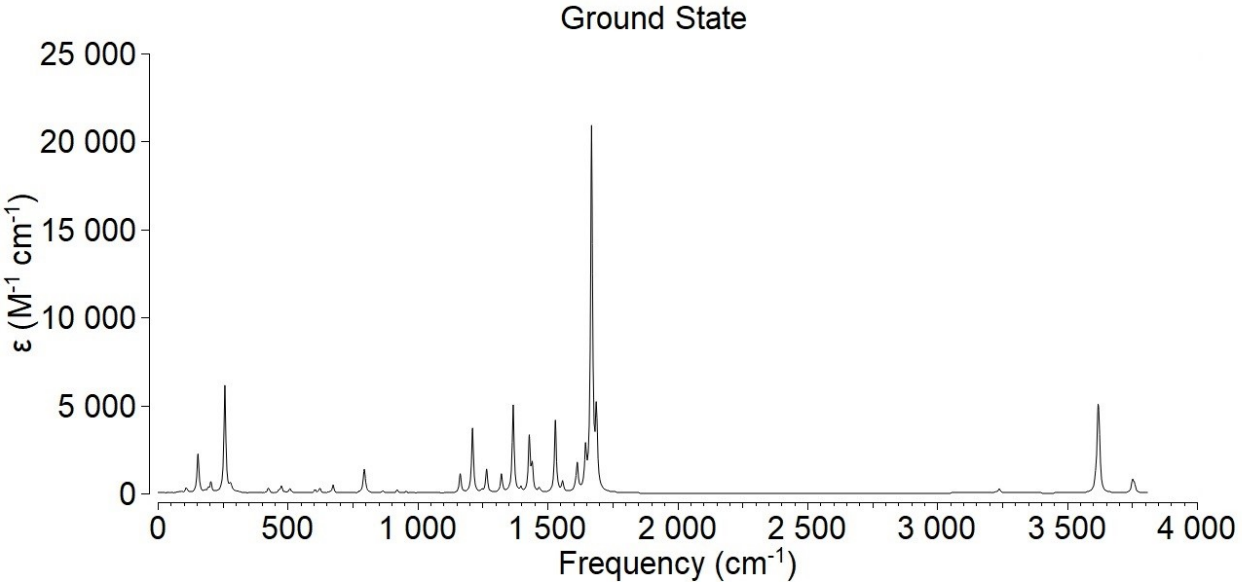

Fig. S66. Calculated vibrational spectra of PF dimer (B2PLYP functional with GD2 correction)

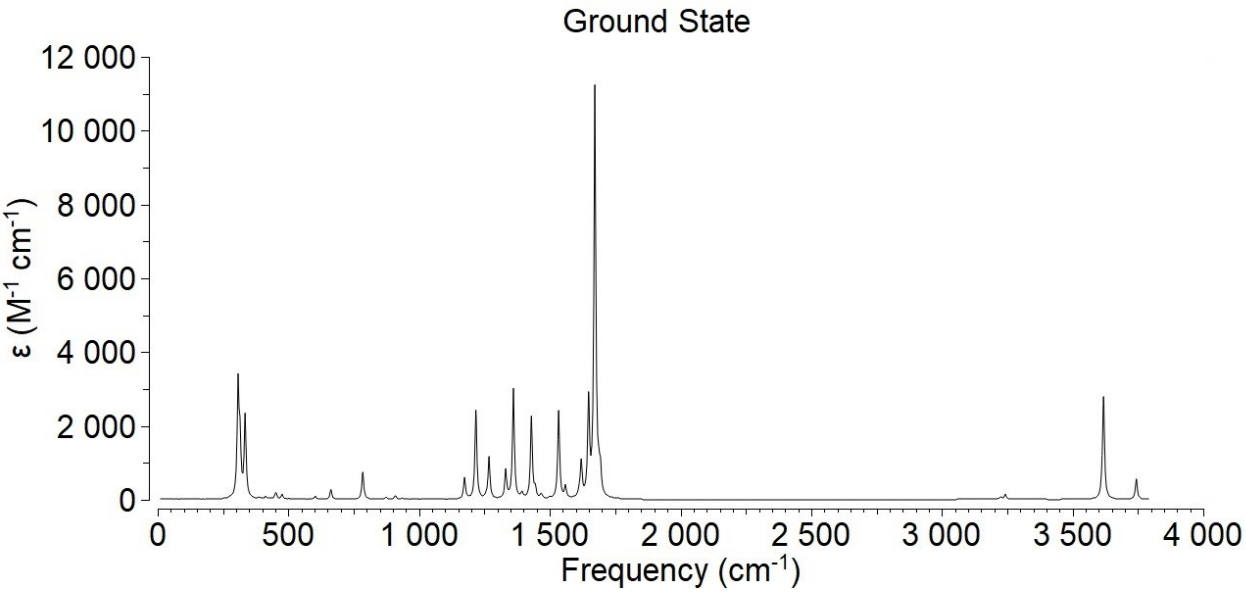

Fig. S67. Calculated vibrational spectra of PF monomer (B2PLYP functional with GD3 correction)

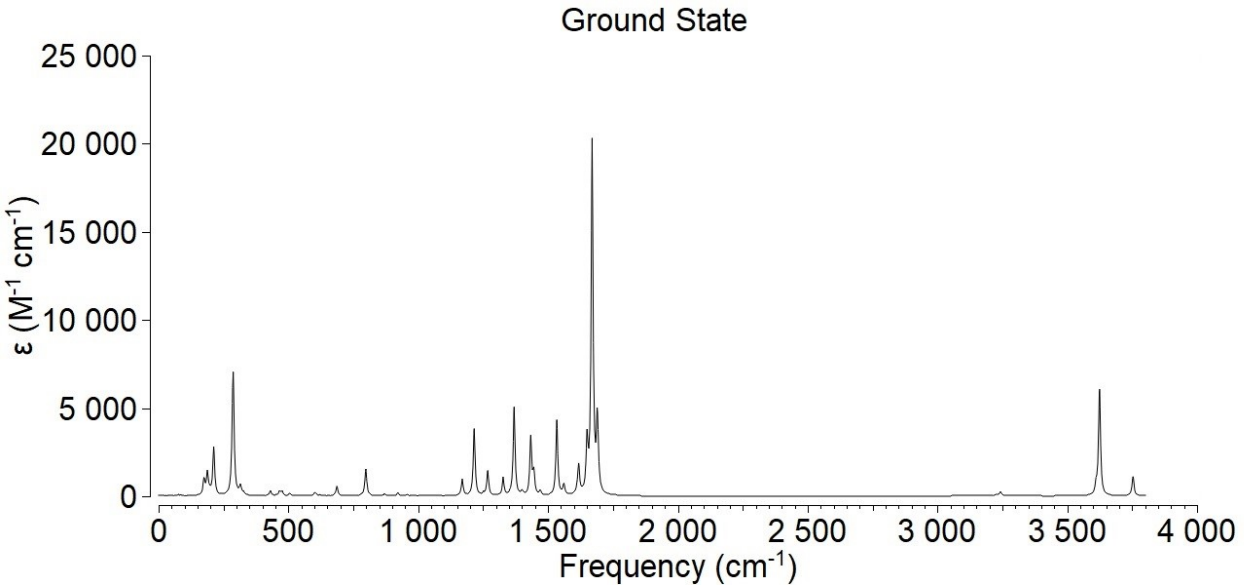

Fig. S68. Calculated vibrational spectra of PF dimer (B2PLYP functional with GD3 correction)

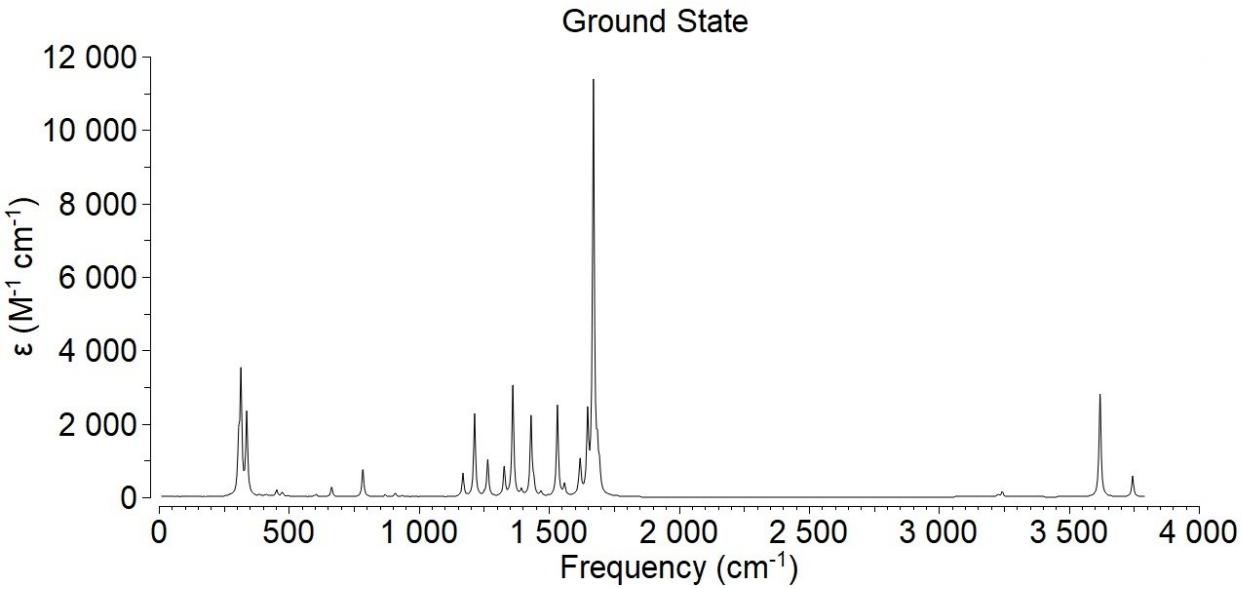

Fig. S69. Calculated vibrational spectra of PF monomer (B2PLYP functional with GD3+BJ correction)

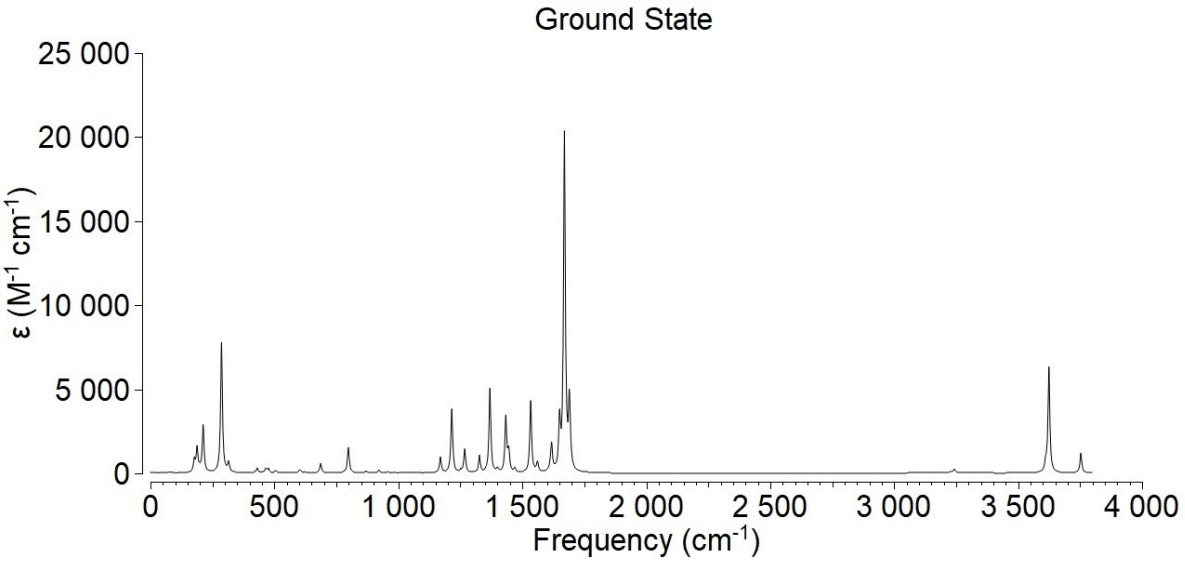

Fig. S70. Calculated vibrational spectra of PF dimer (B2PLYP functional with GD3+BJ correction)

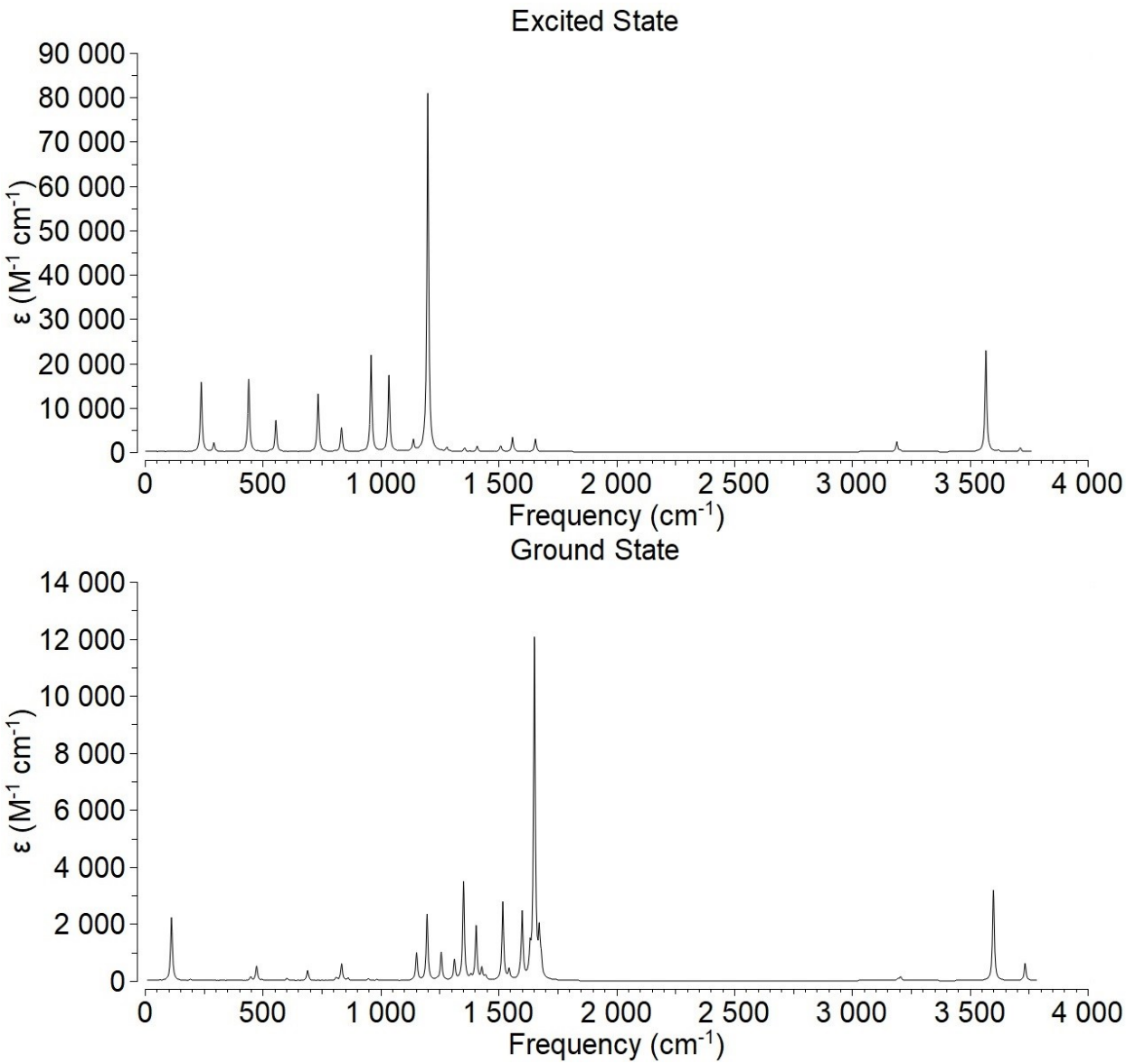

Fig. S71. Calculated vibrational spectra of PF monomer (B3LYP functional with GD2 correction)

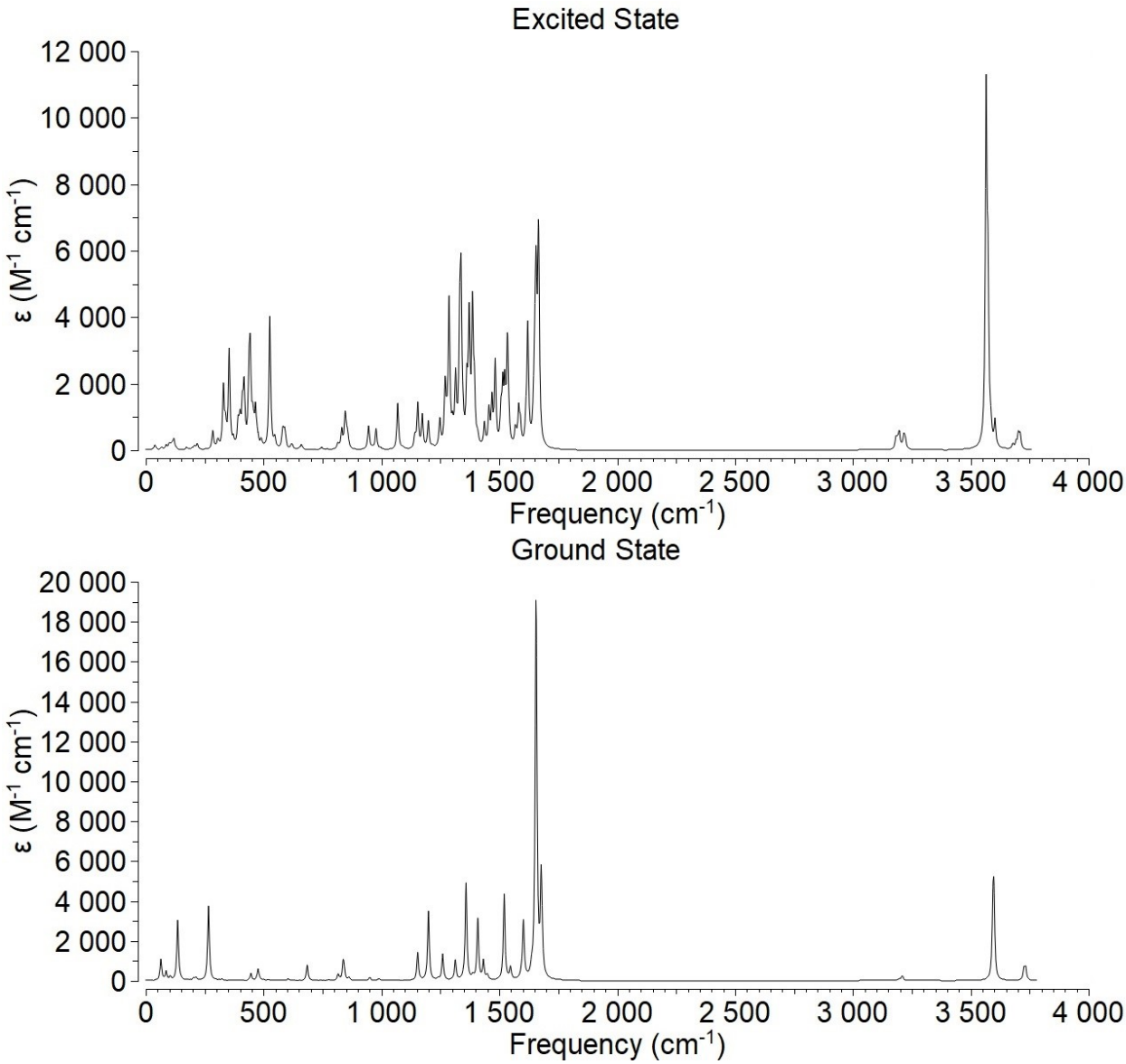

Fig. S72. Calculated vibrational spectra of PF dimer (B3LYP functional with GD2 correction)

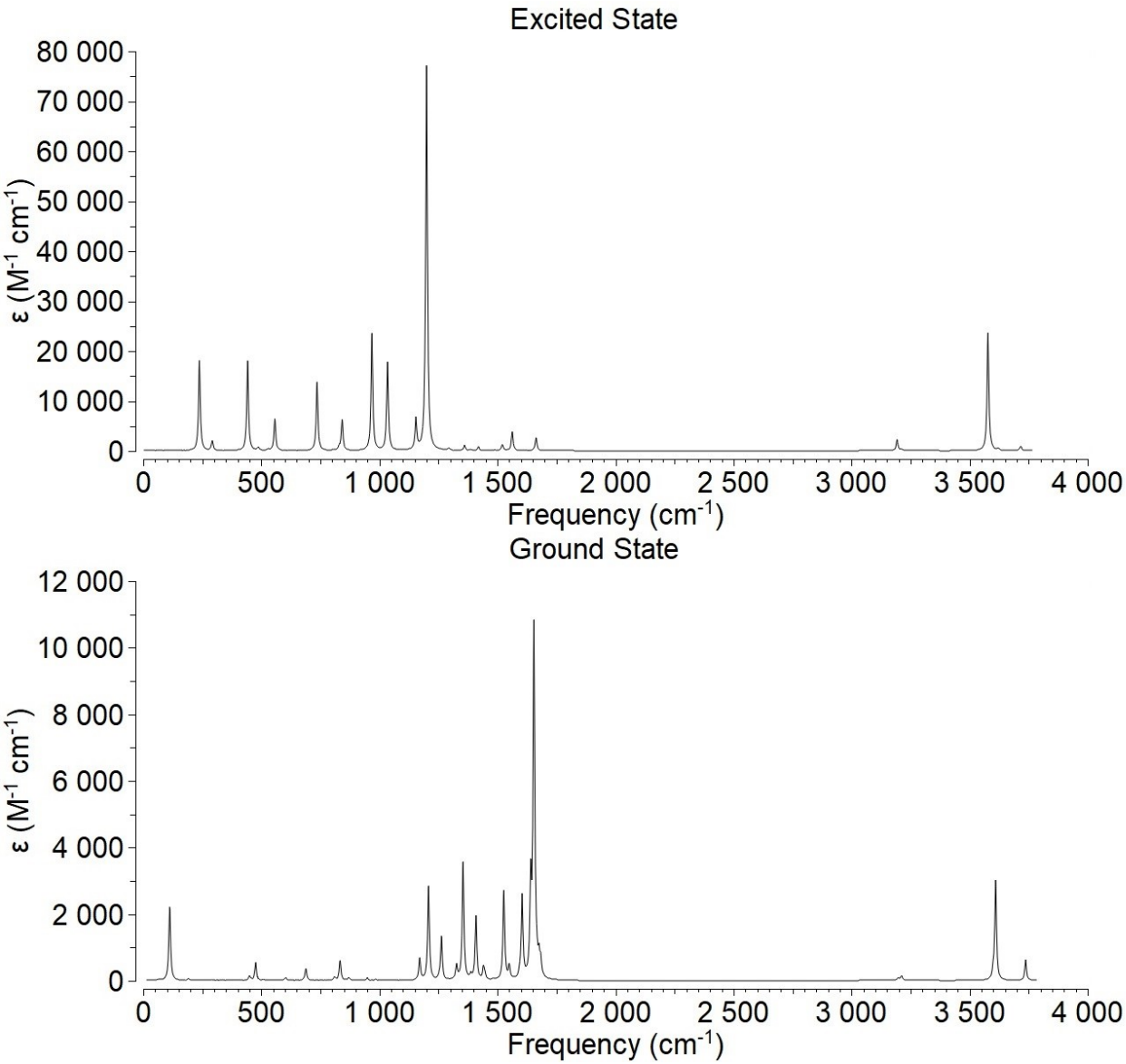

Fig. S73. Calculated vibrational spectra of PF monomer (B3LYP functional with GD3 correction)

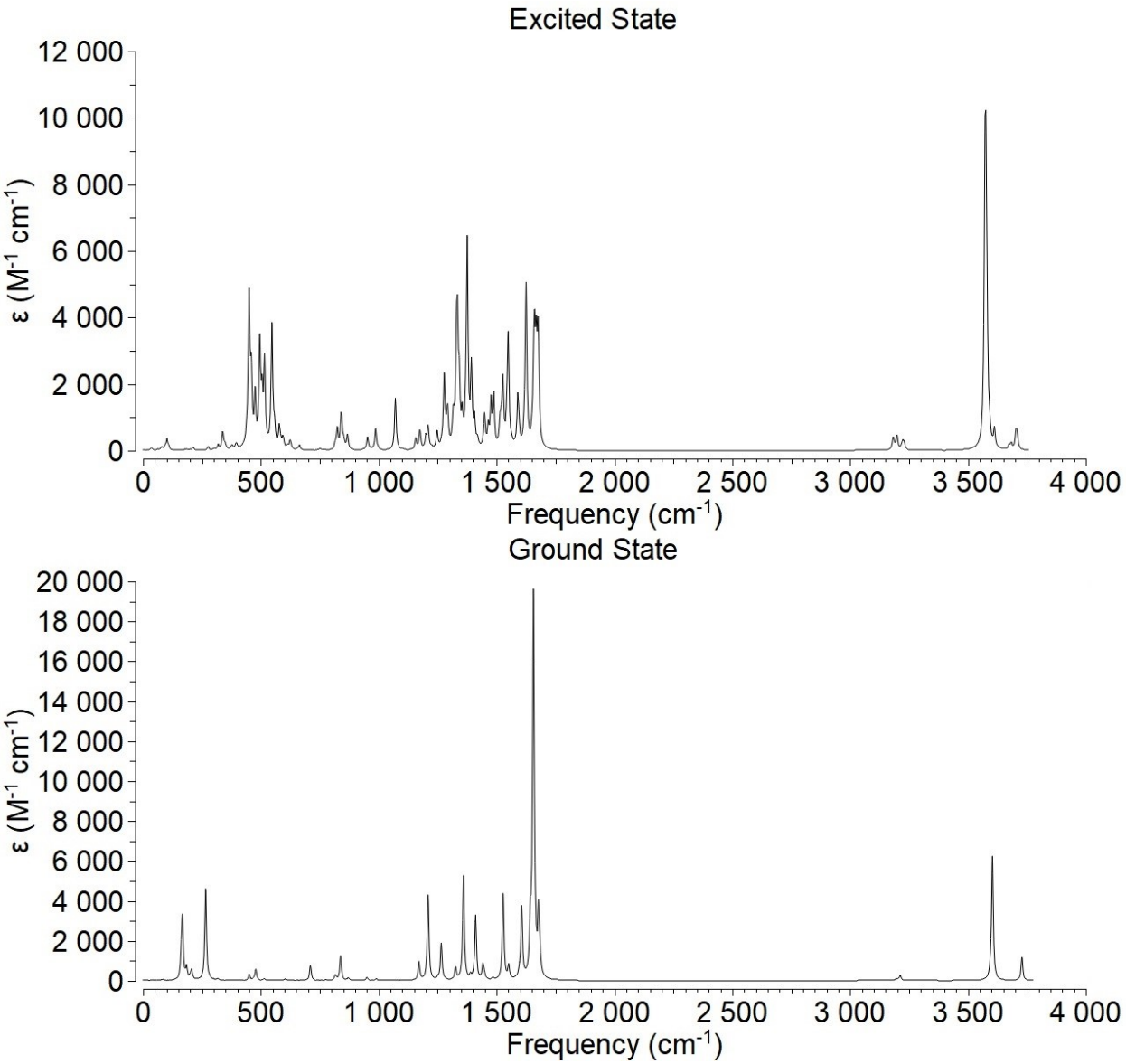

Fig. S74. Calculated vibrational spectra of PF dimer (B3LYP functional with GD3 correction)

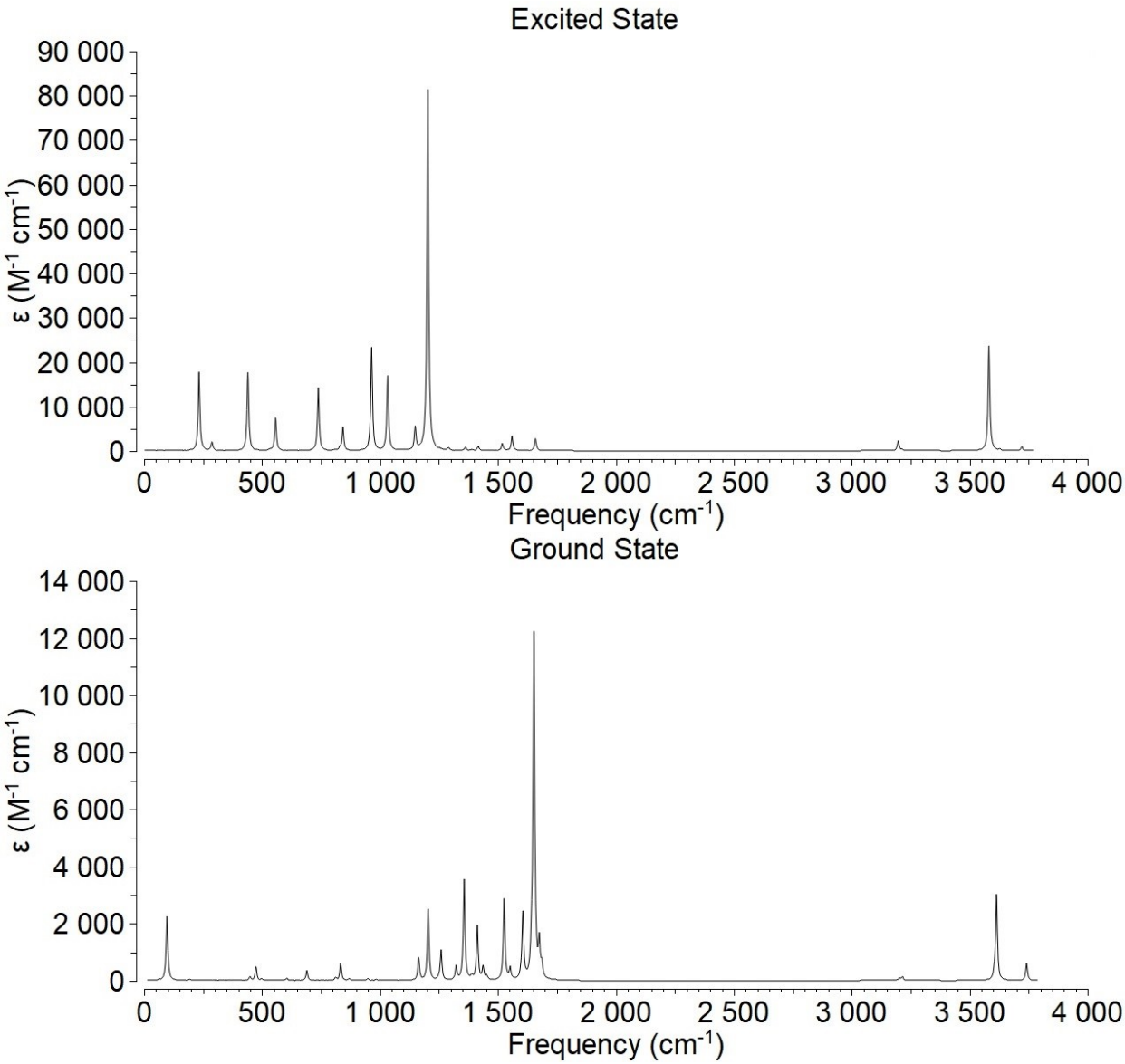

Fig. S75. Calculated vibrational spectra of PF monomer (B3LYP functional with GD3+BJ correction)

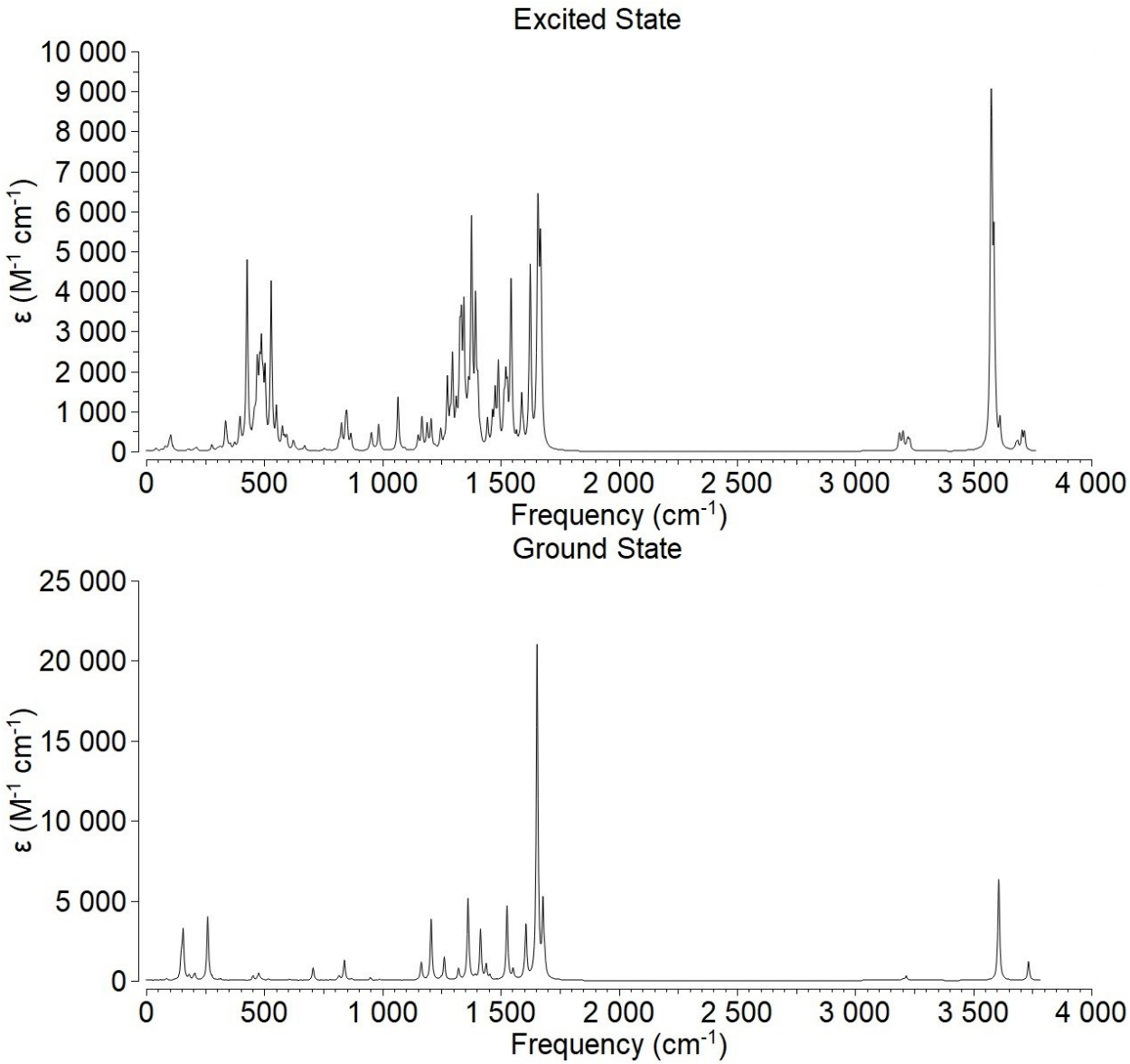

Fig. S76. Calculated vibrational spectra of PF dimer (B3LYP functional with GD3+BJ correction)

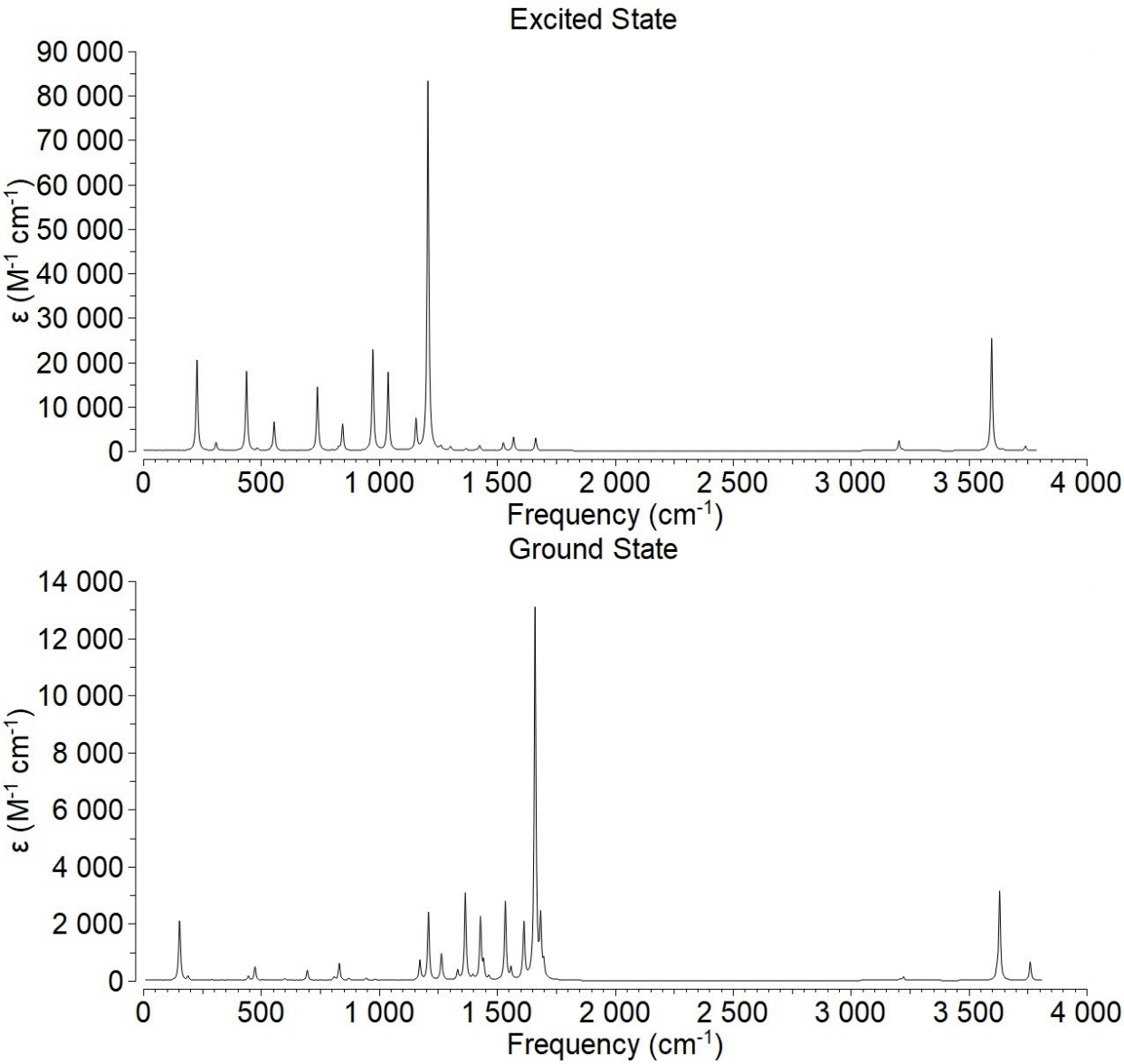

Fig. S77. Calculated vibrational spectra of PF monomer (B3PW91 functional with GD3 correction)

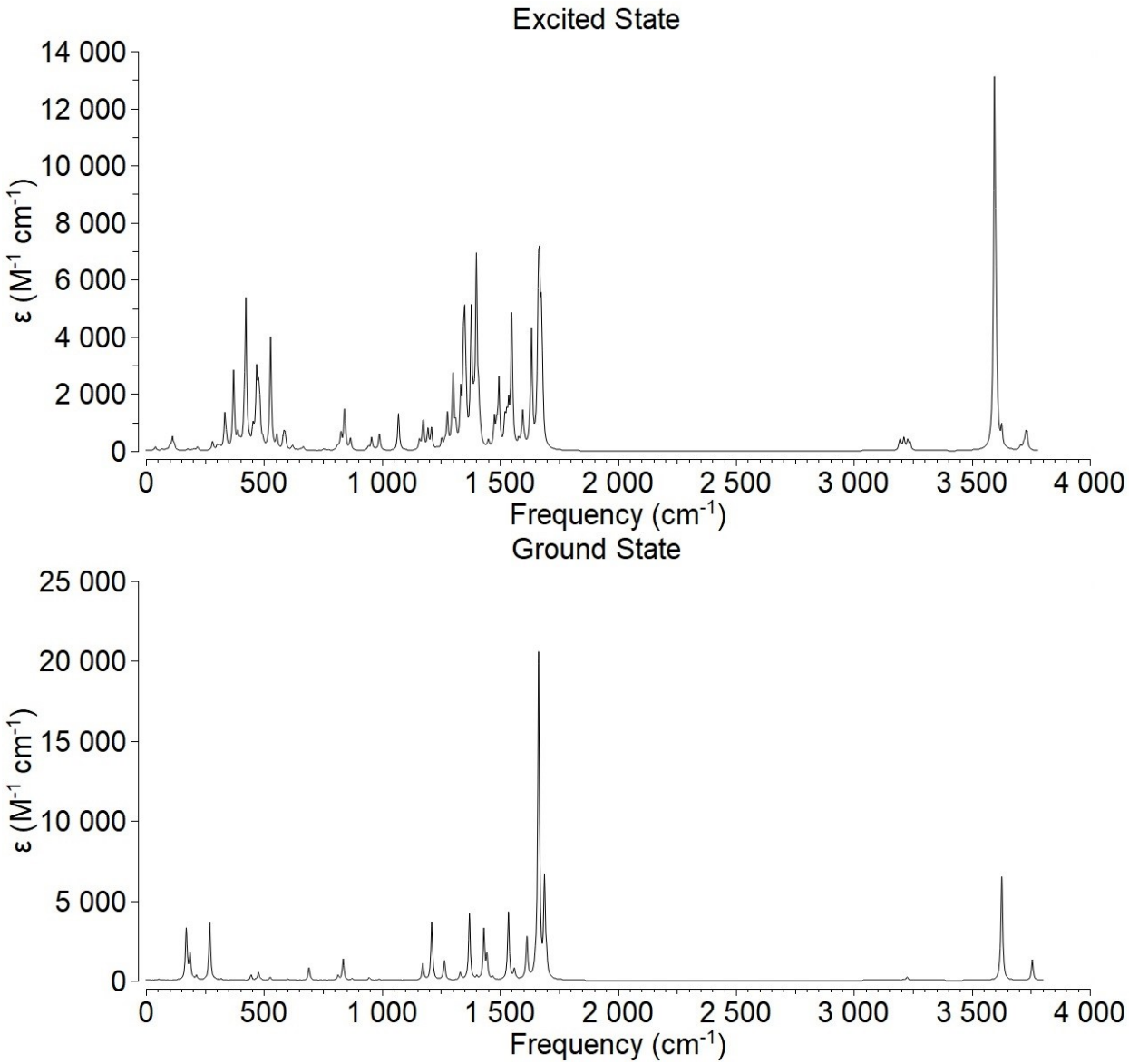

Fig. S78. Calculated vibrational spectra of PF dimer (B3PW91 functional with GD3 correction)

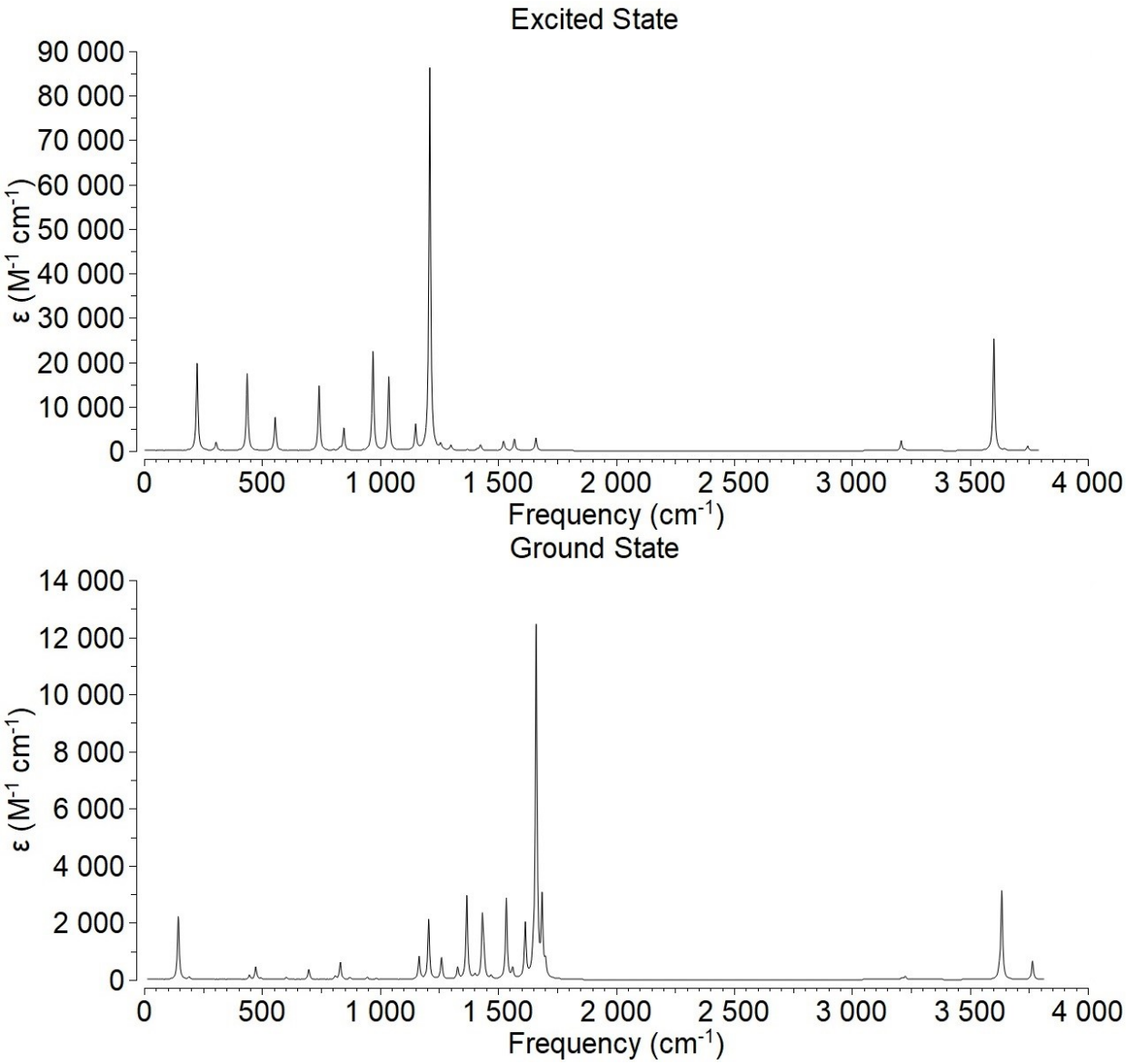

Fig. S79. Calculated vibrational spectra of PF monomer (B3PW91 functional with GD3+BJ correction)

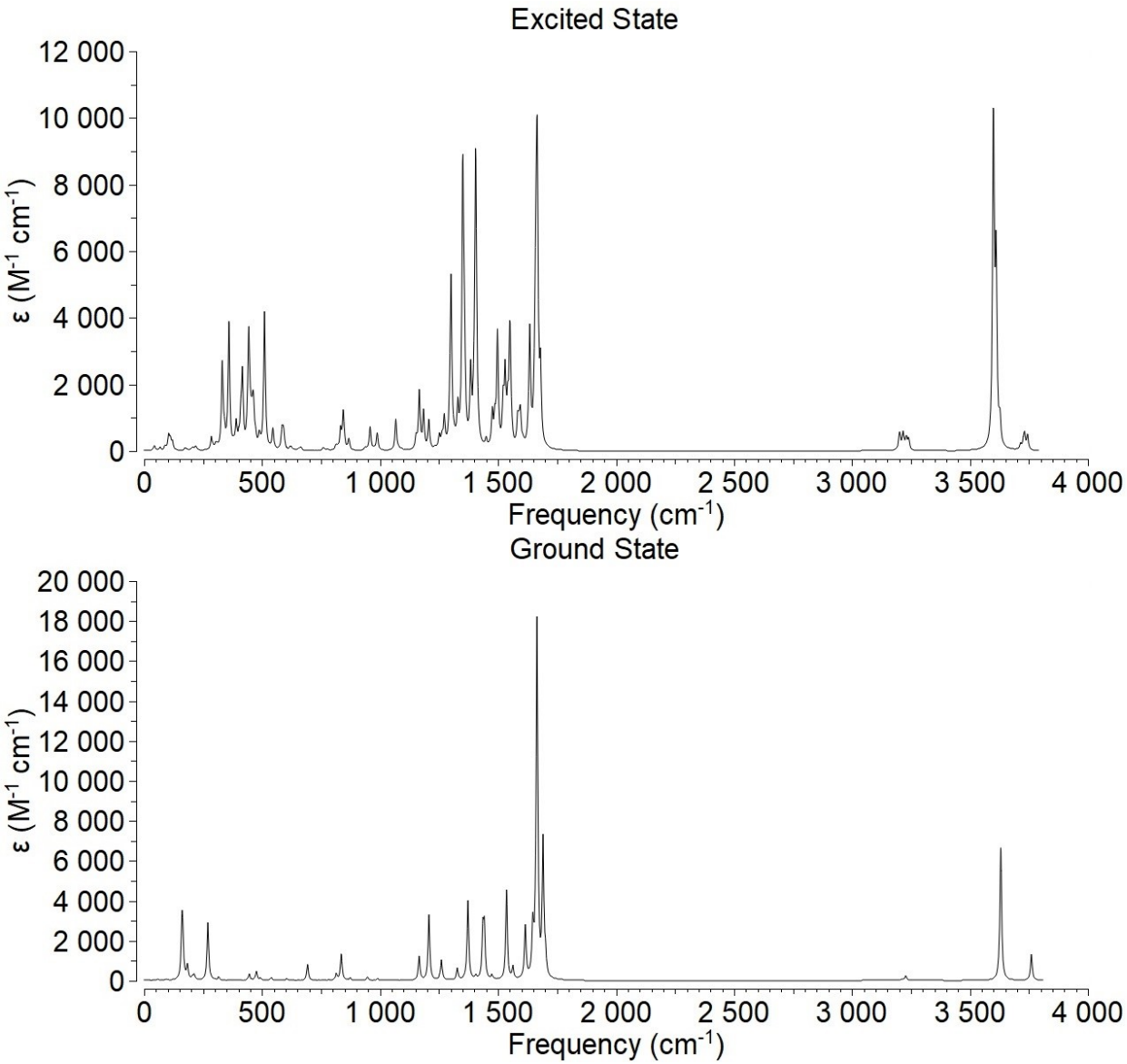

Fig. S80. Calculated vibrational spectra of PF dimer (B3PW91 functional with GD3+BJ correction)

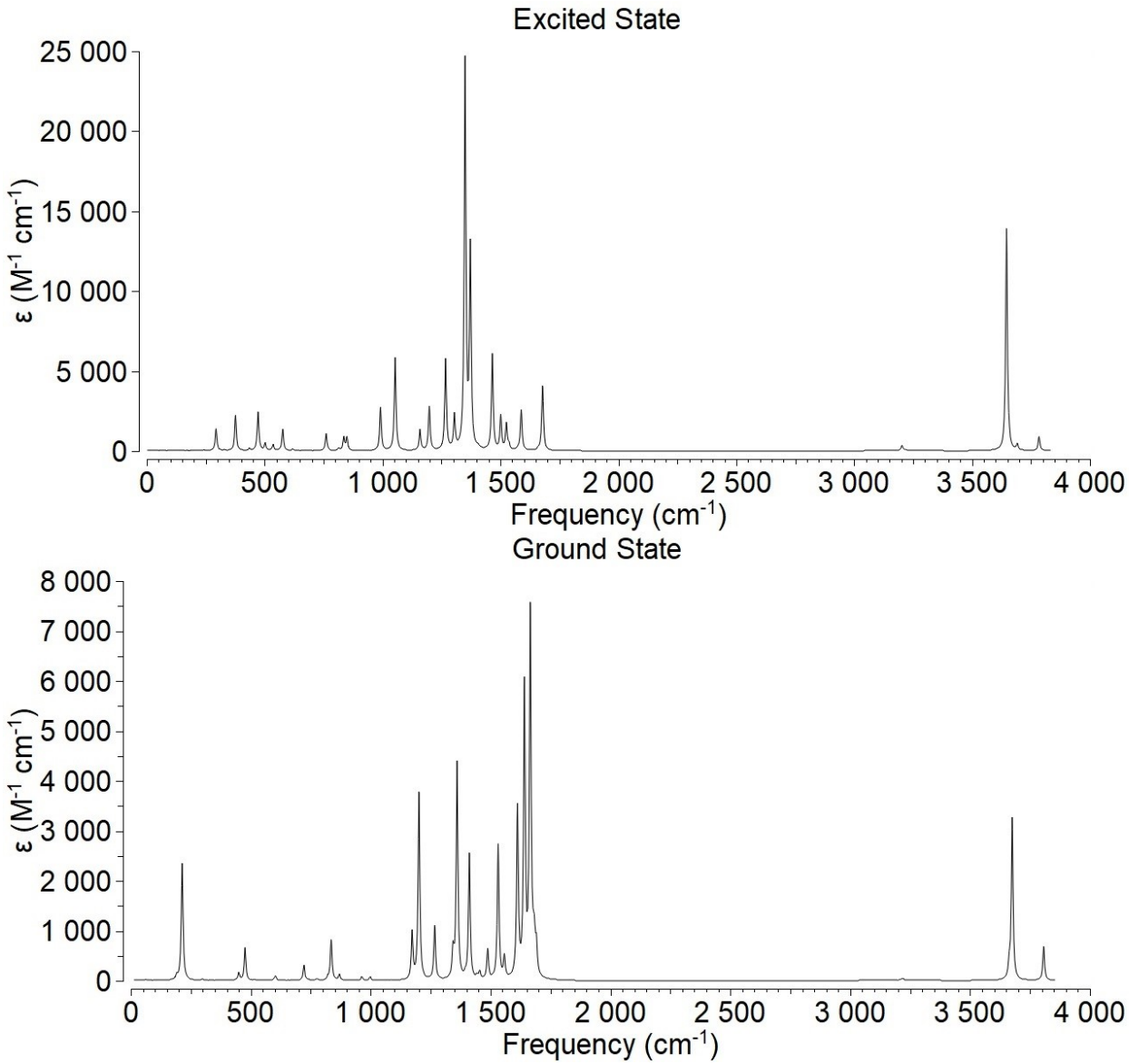

Fig. S81. Calculated vibrational spectra of PF monomer (BMK functional with GD3 correction)

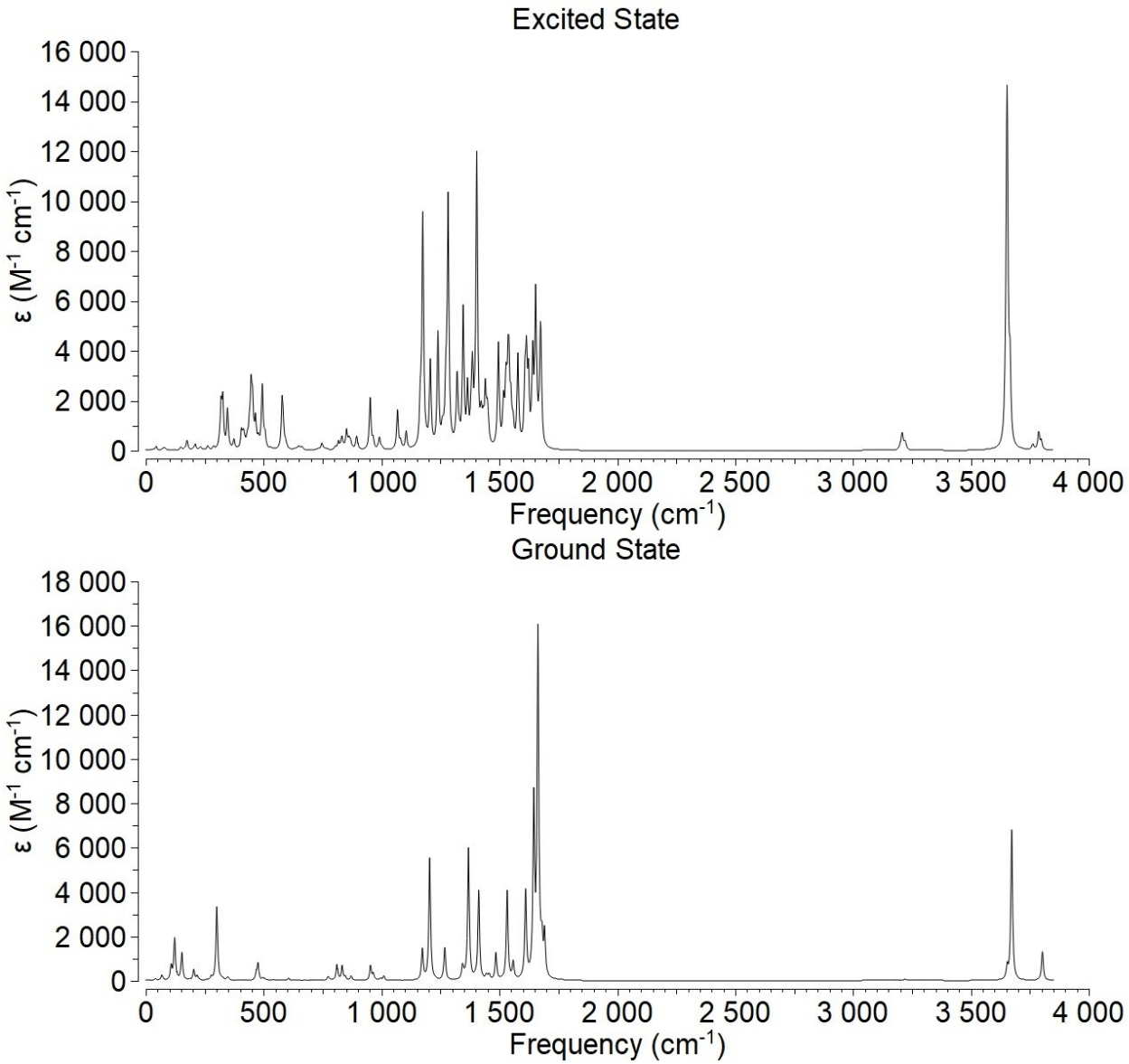

Fig. S82. Calculated vibrational spectra of PF dimer (BMK functional with GD3 correction)

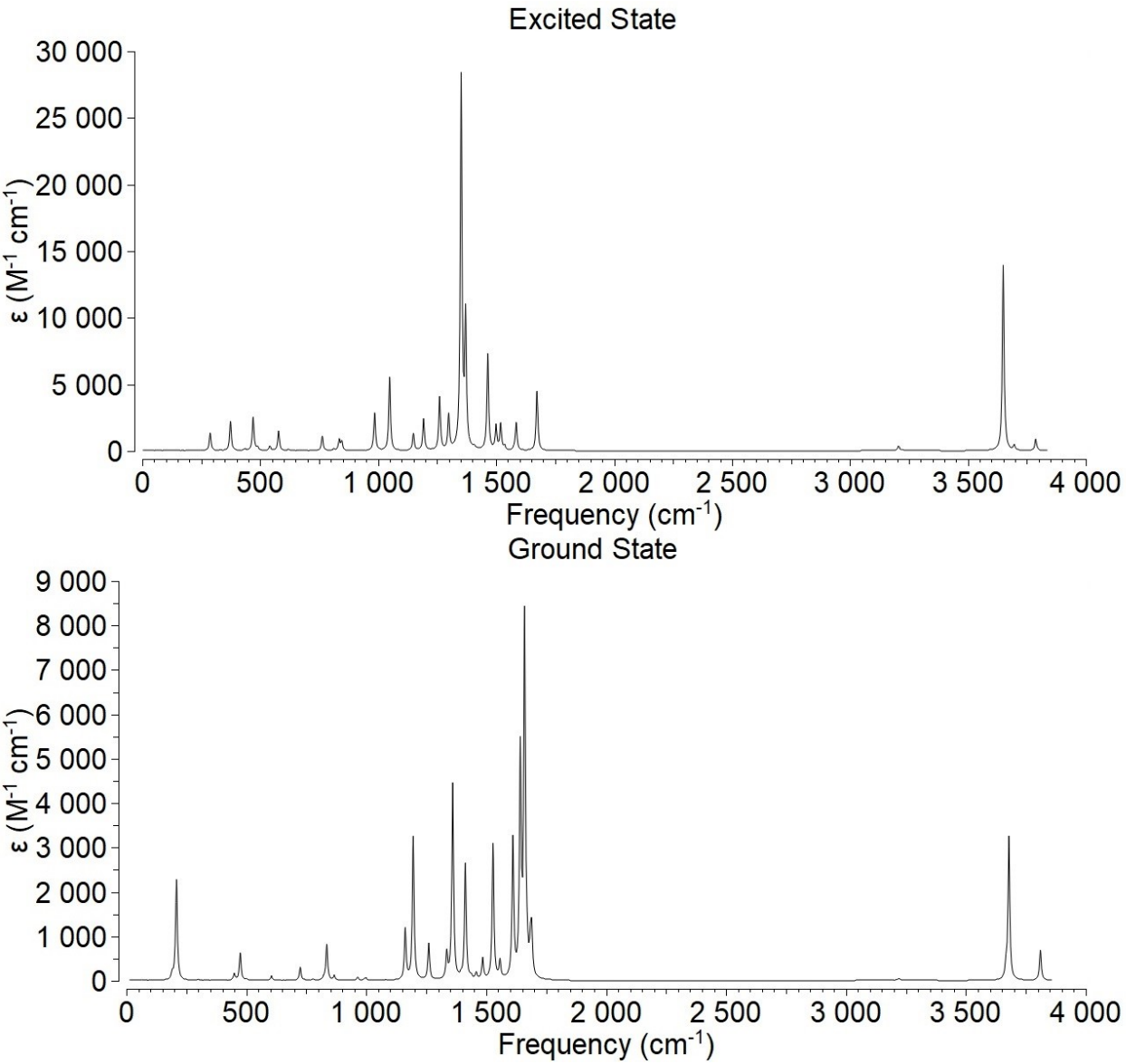

Fig. S83. Calculated vibrational spectra of PF monomer (BMK functional with GD3+BJ correction)

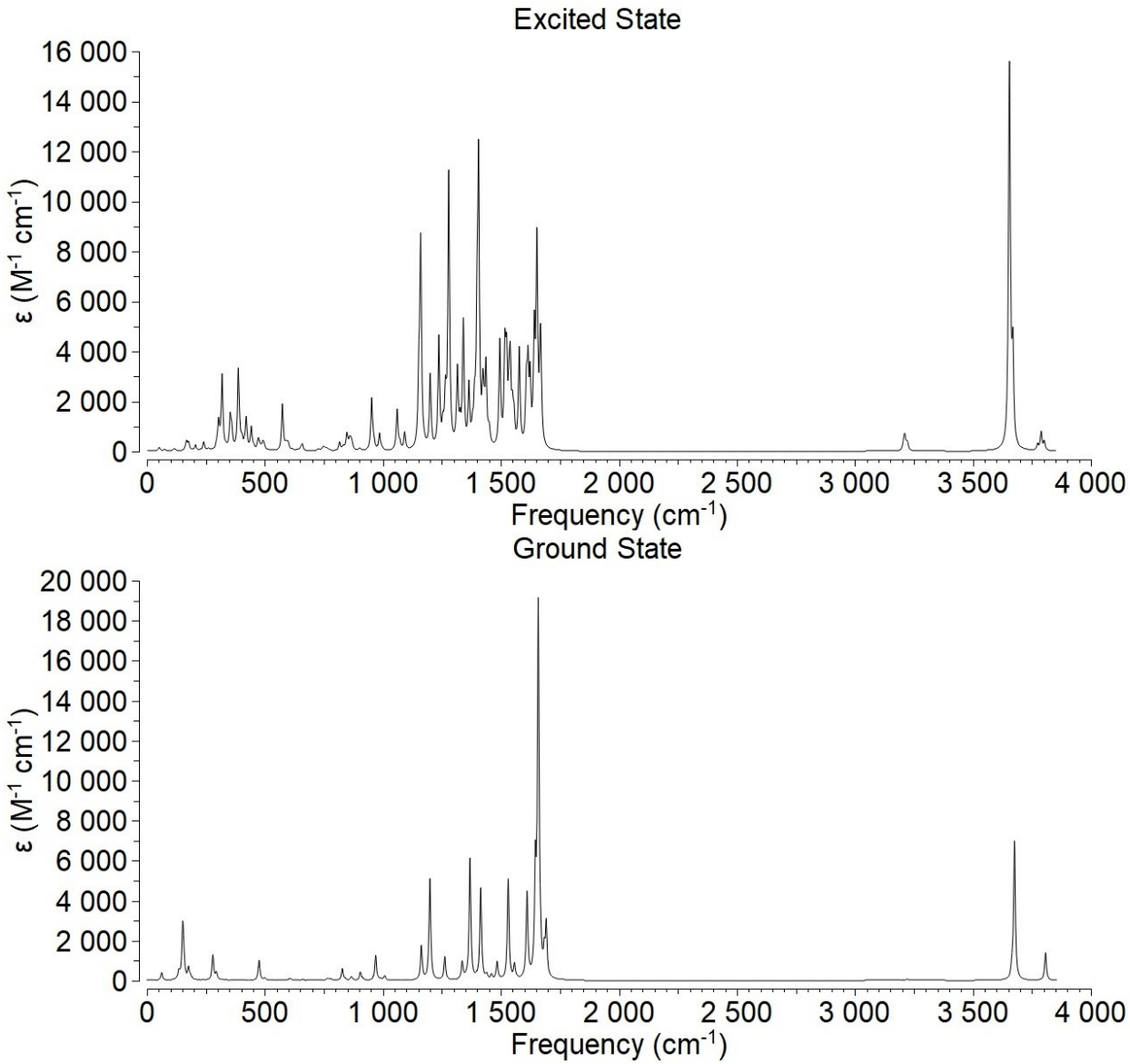

Fig. S84. Calculated vibrational spectra of PF dimer (BMK functional with GD3+BJ correction)

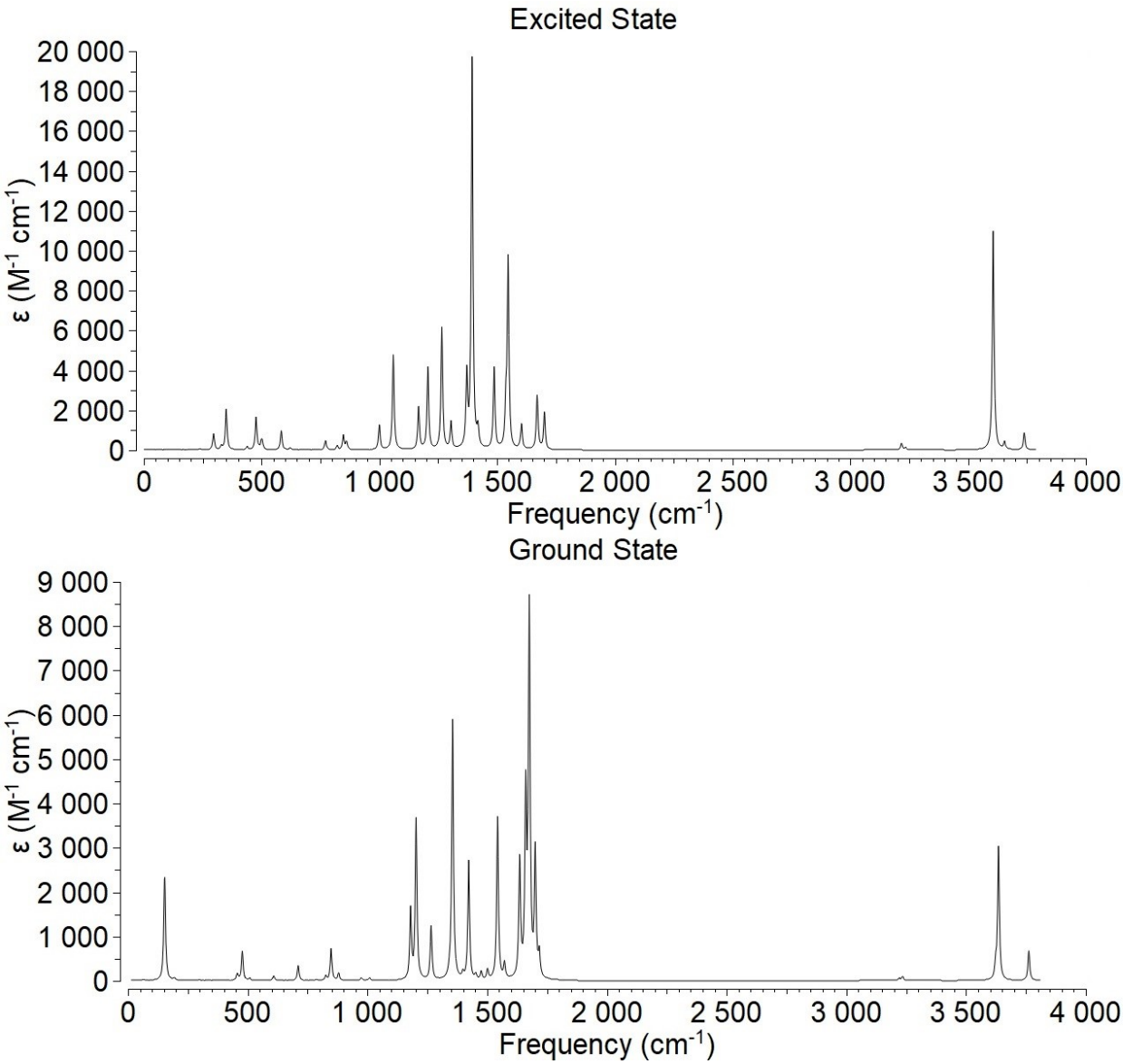

Fig. S85. Calculated vibrational spectra of PF monomer (CAM-B3LYP functional with GD3 correction)

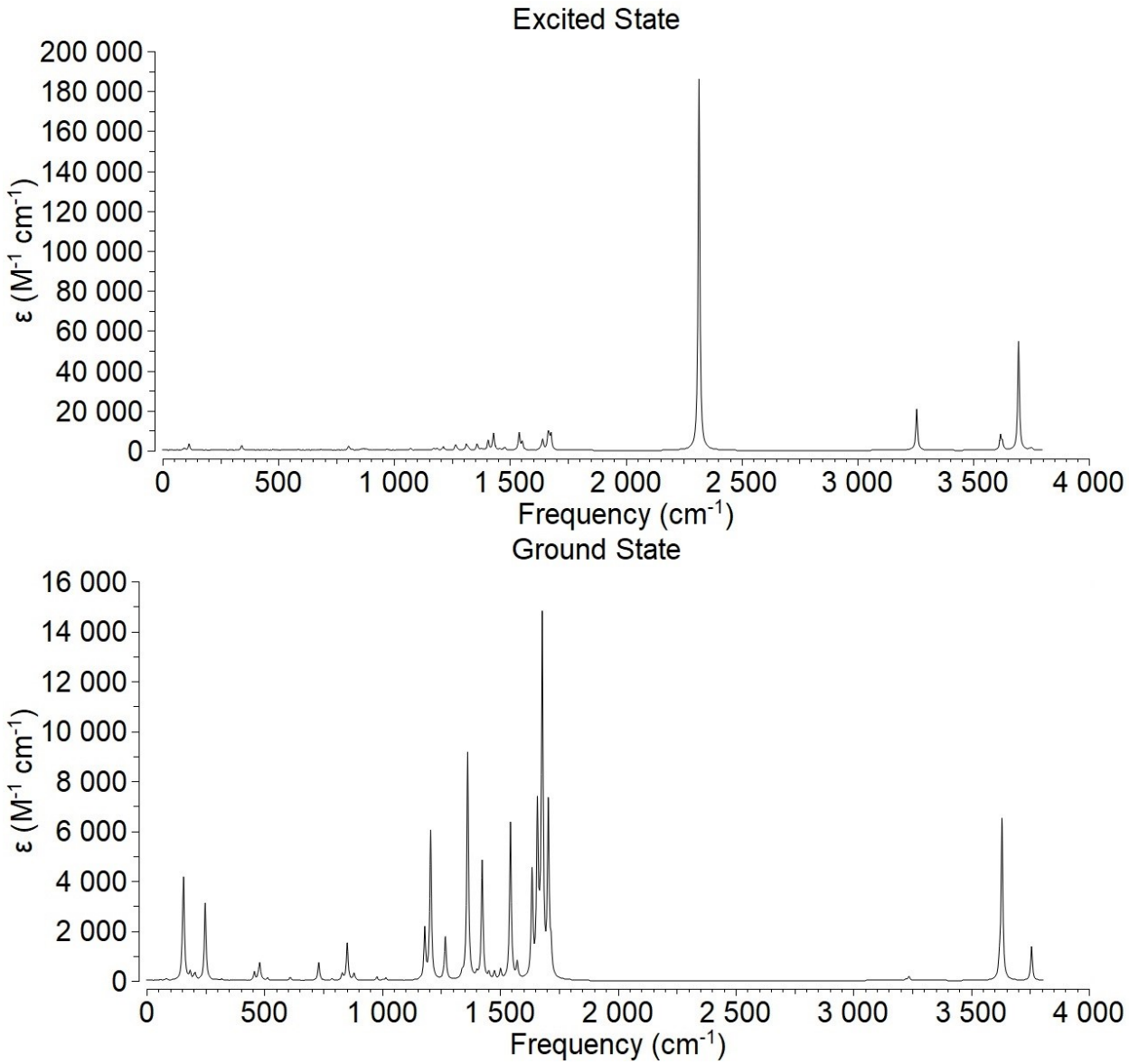

Fig. S86. Calculated vibrational spectra of PF dimer (CAM-B3LYP functional with GD3 correction)

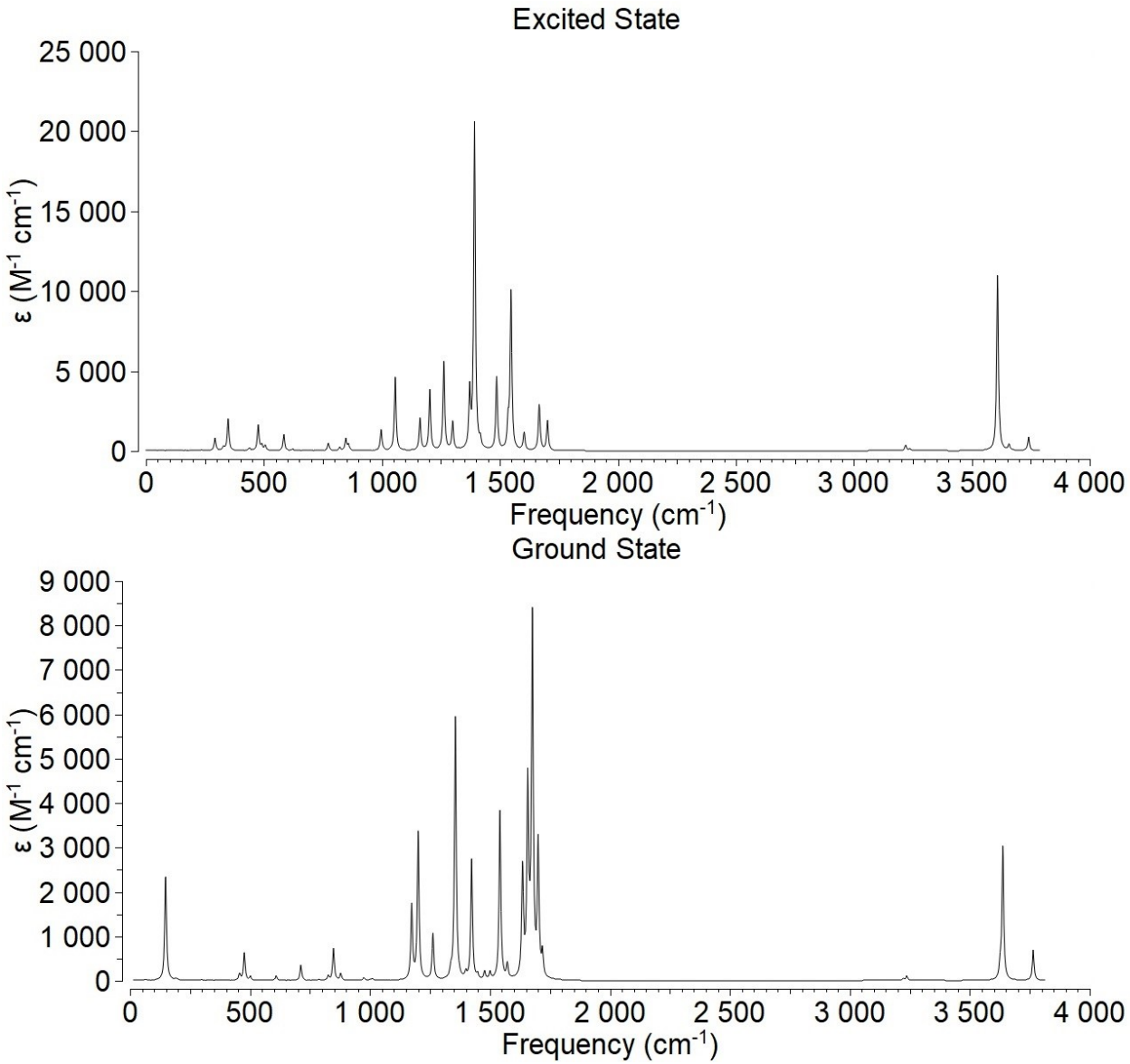

Fig. S87. Calculated vibrational spectra of PF monomer (CAM-B3LYP functional with GD3+BJ correction)

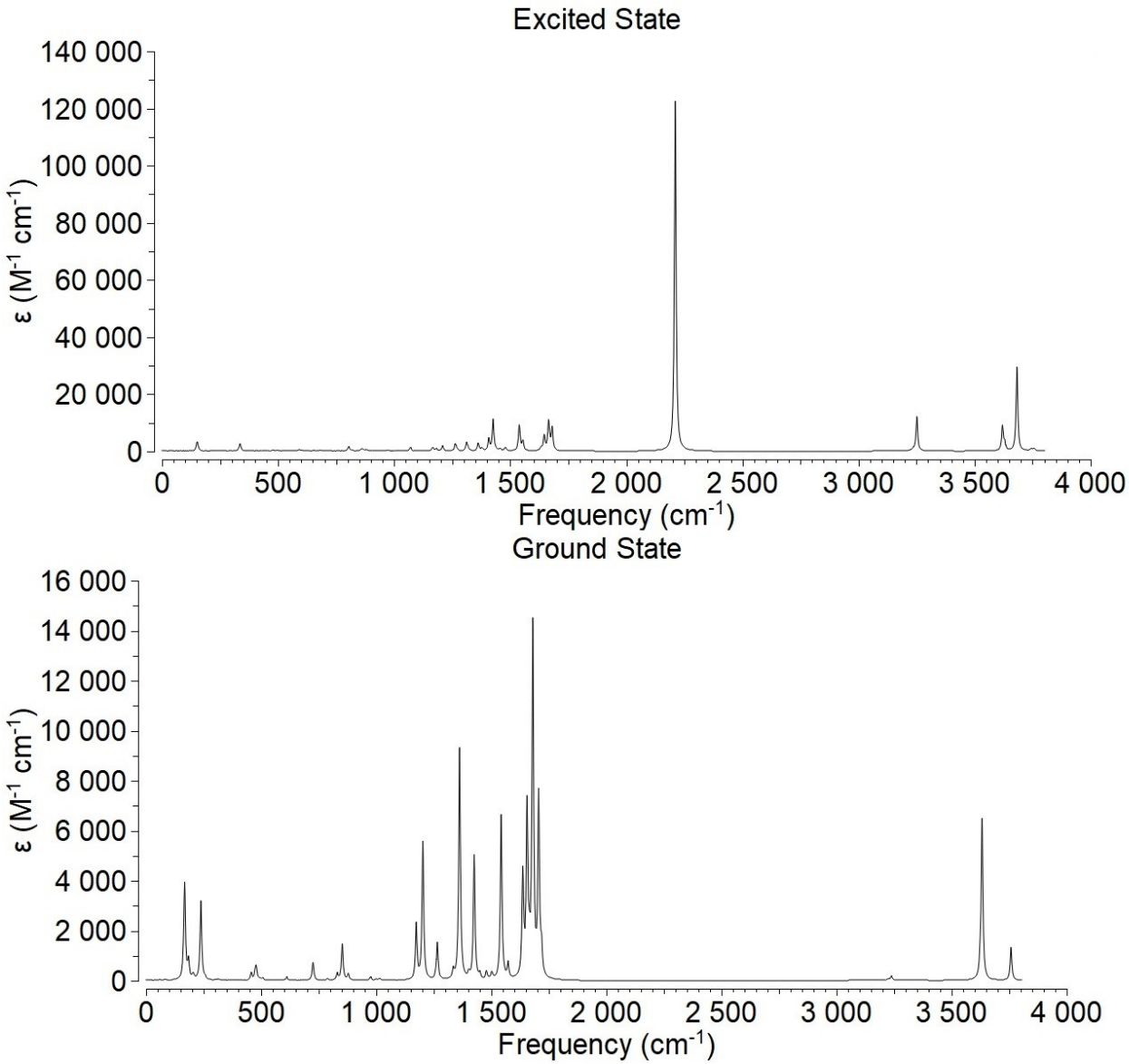

Fig. S88. Calculated vibrational spectra of PF dimer (CAM-B3LYP functional with GD3+BJ correction)

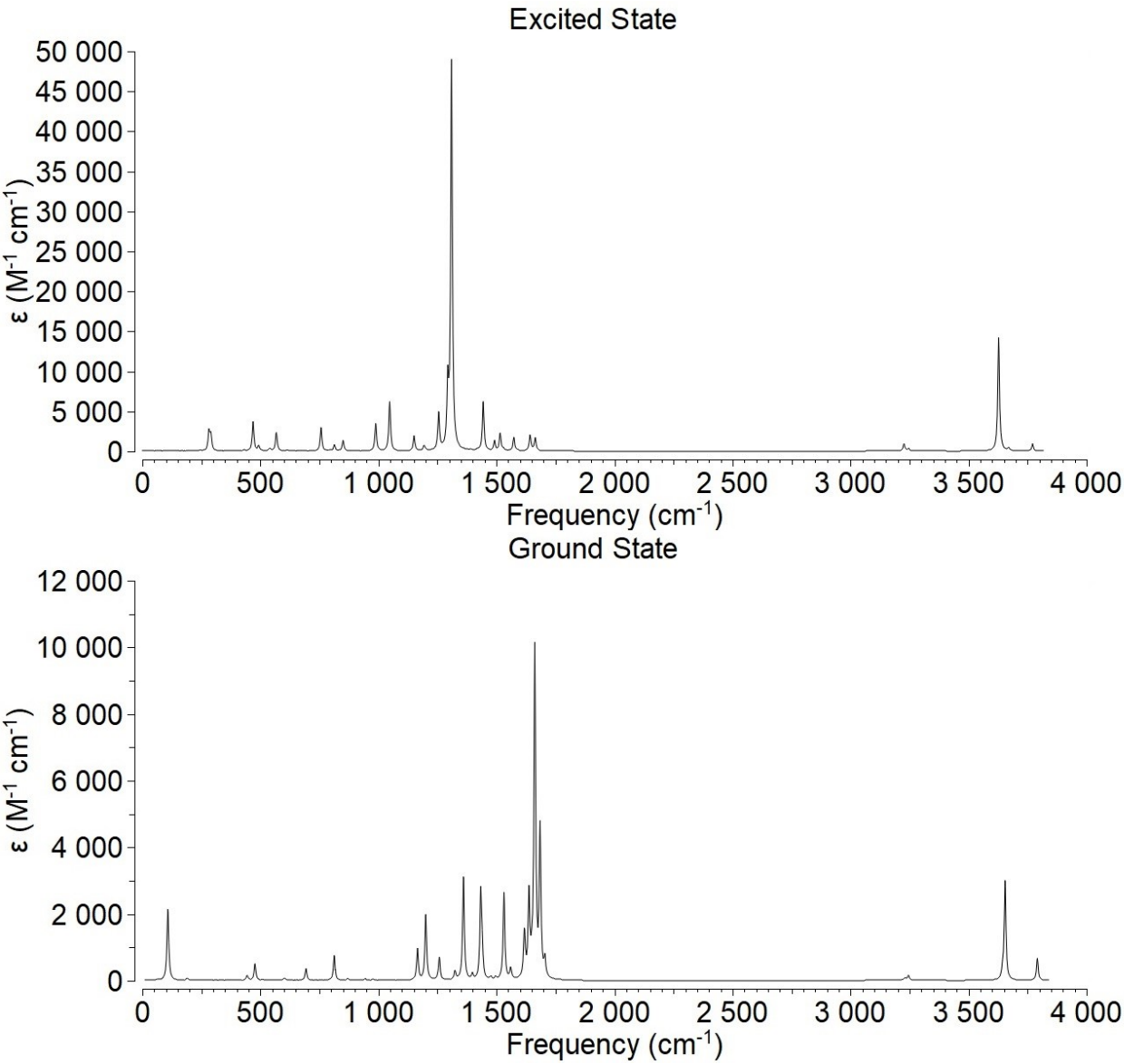

Fig. S89. Calculated vibrational spectra of PF monomer (M05 functional with GD3 correction)

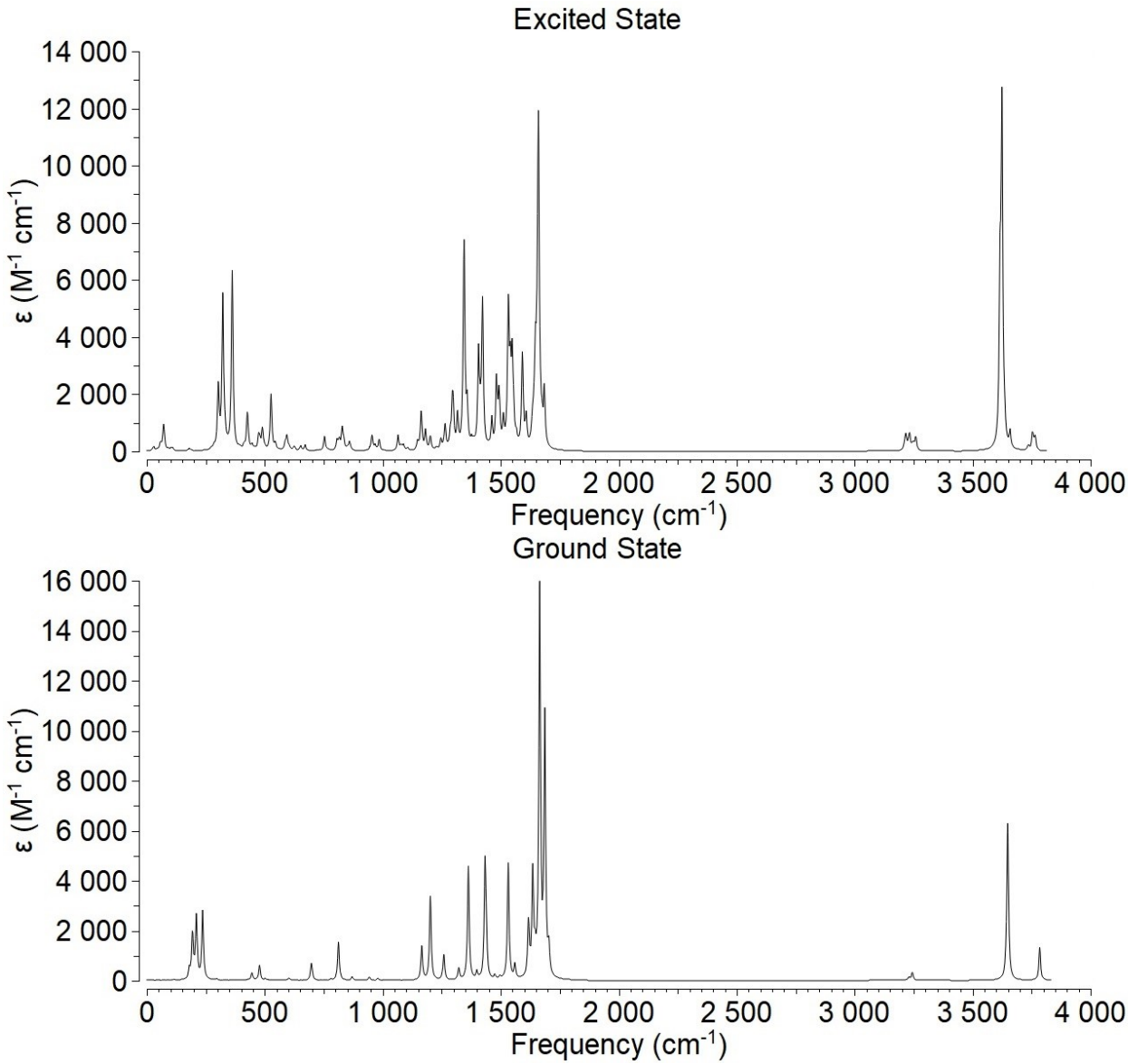

Fig. S90. Calculated vibrational spectra of PF dimer (M05 functional with GD3 correction)

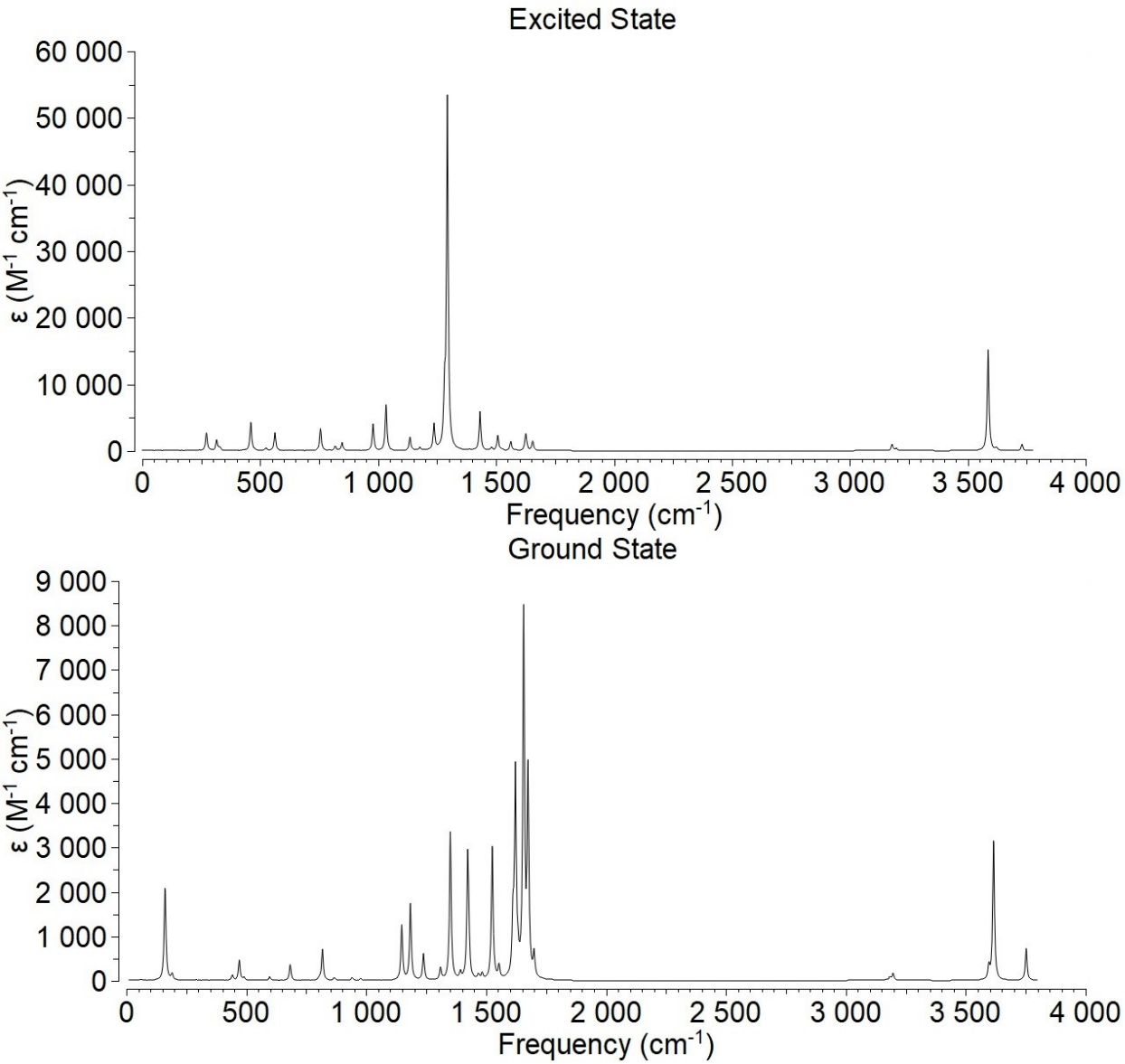

Fig. S91. Calculated vibrational spectra of PF monomer (M06 functional)

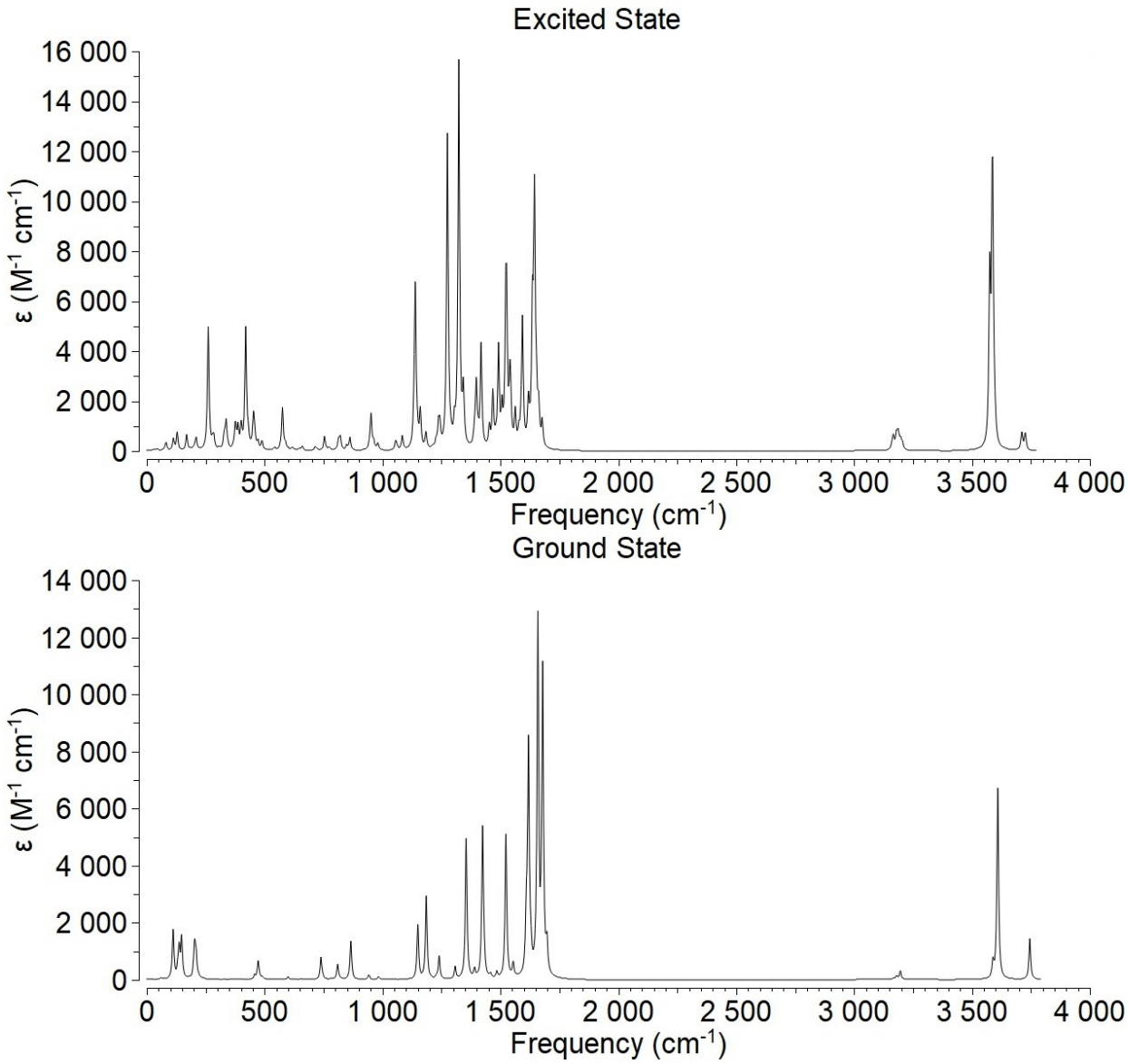

Fig. S92. Calculated vibrational spectra of PF dimer (M06 functional)

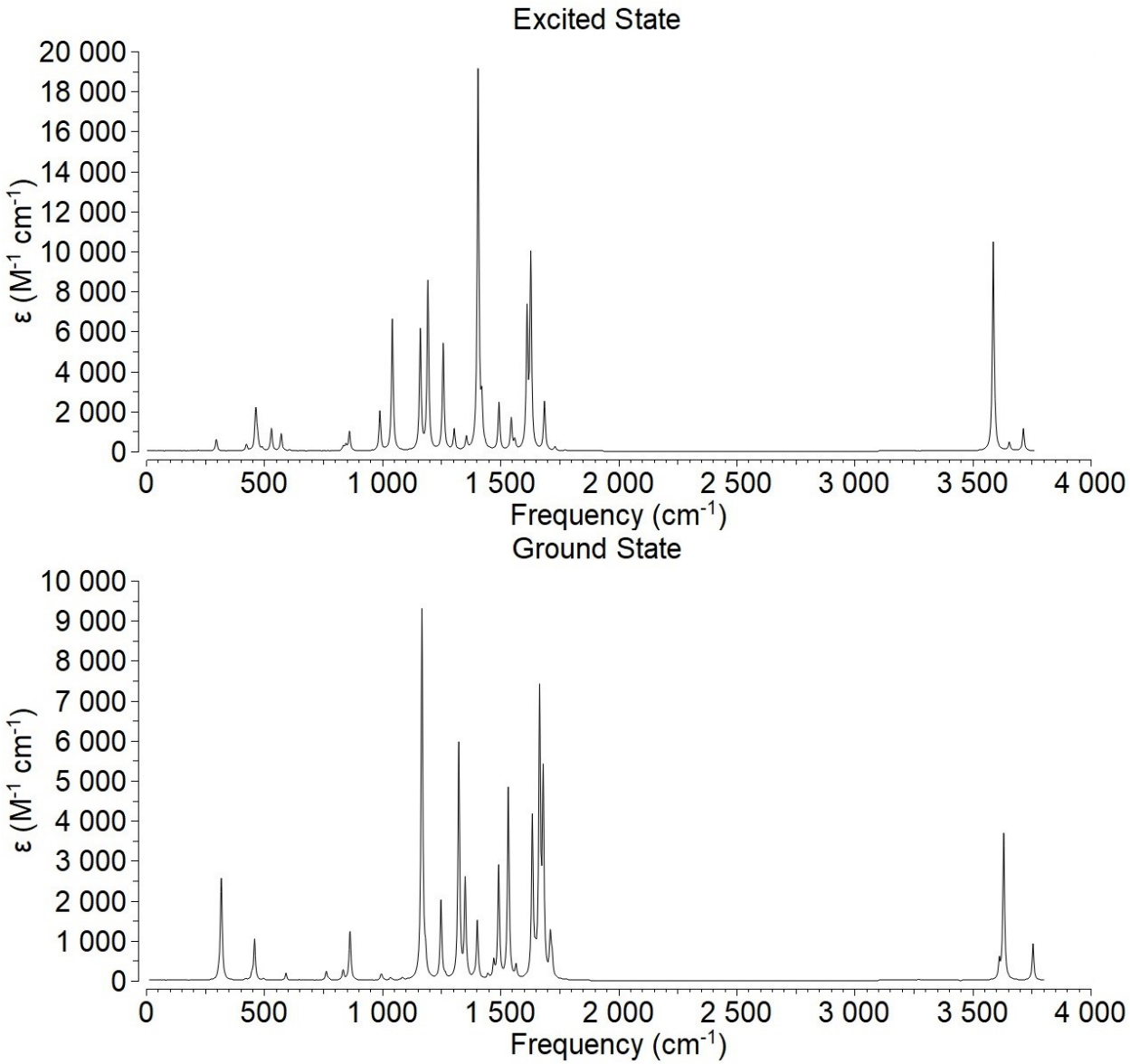

Fig. S93. Calculated vibrational spectra of PF monomer (M06HF functional)

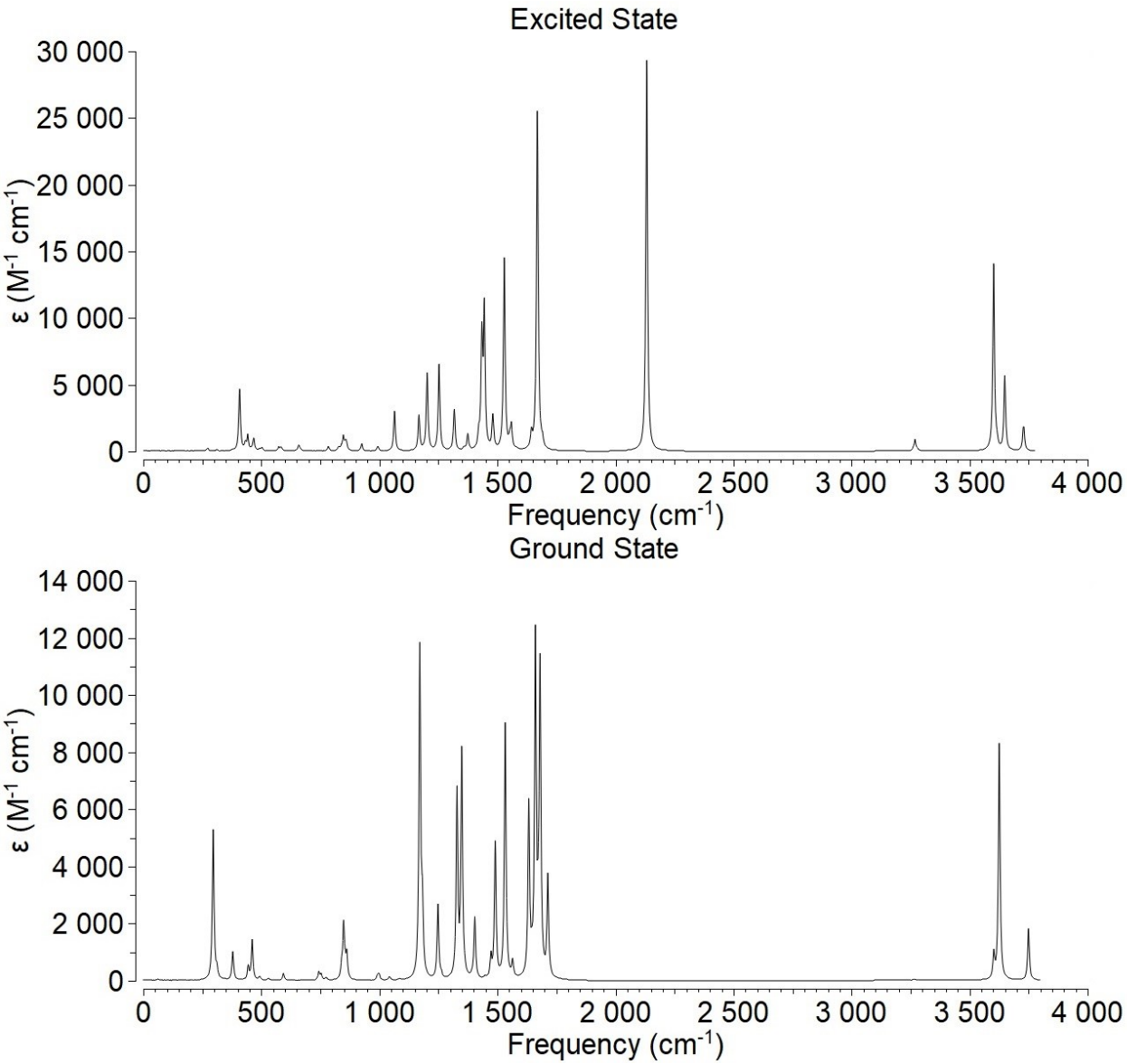

Fig. S94. Calculated vibrational spectra of PF dimer (M06HF functional)

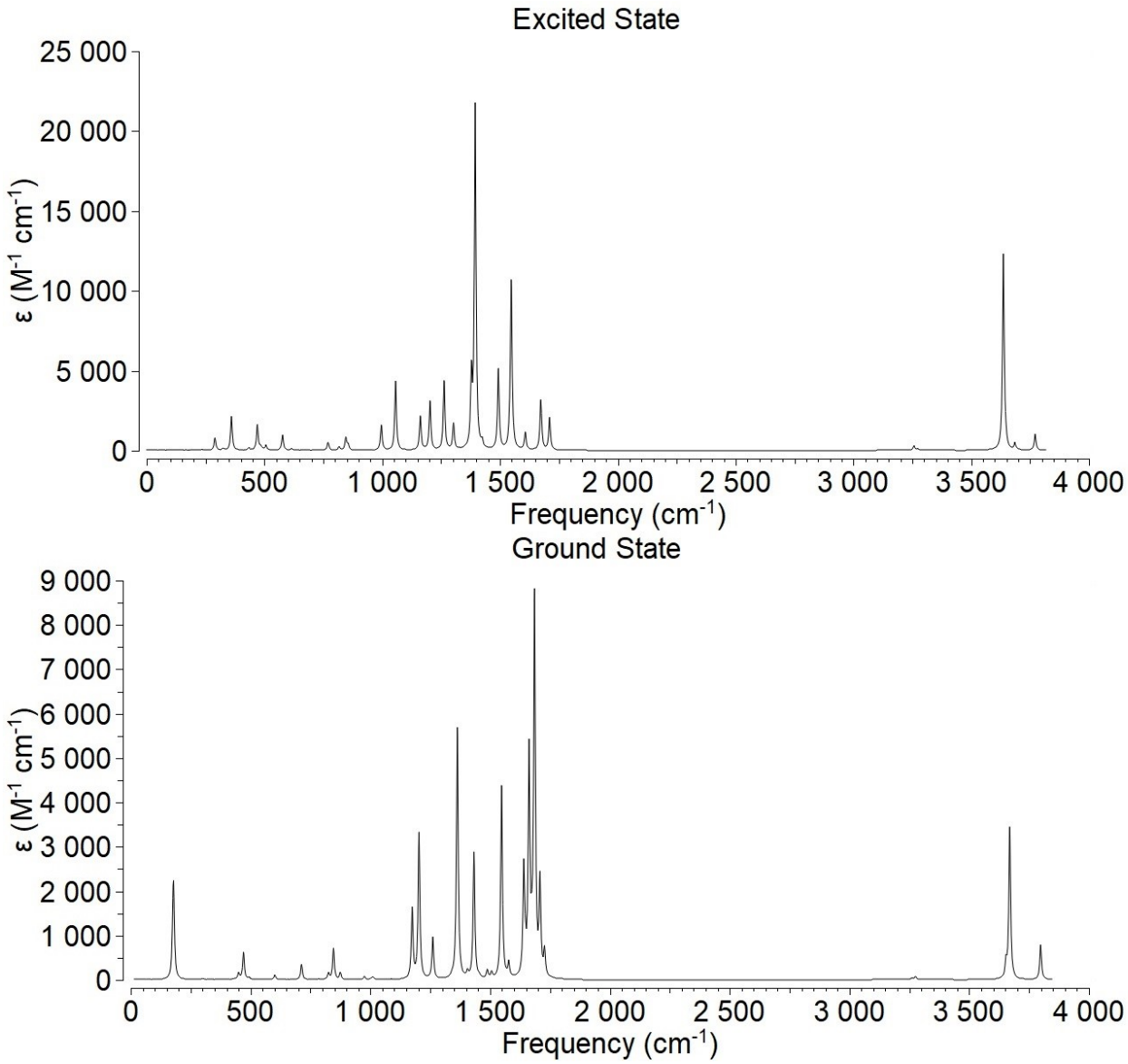

Fig. S95. Calculated vibrational spectra of PF monomer (M052X functional)

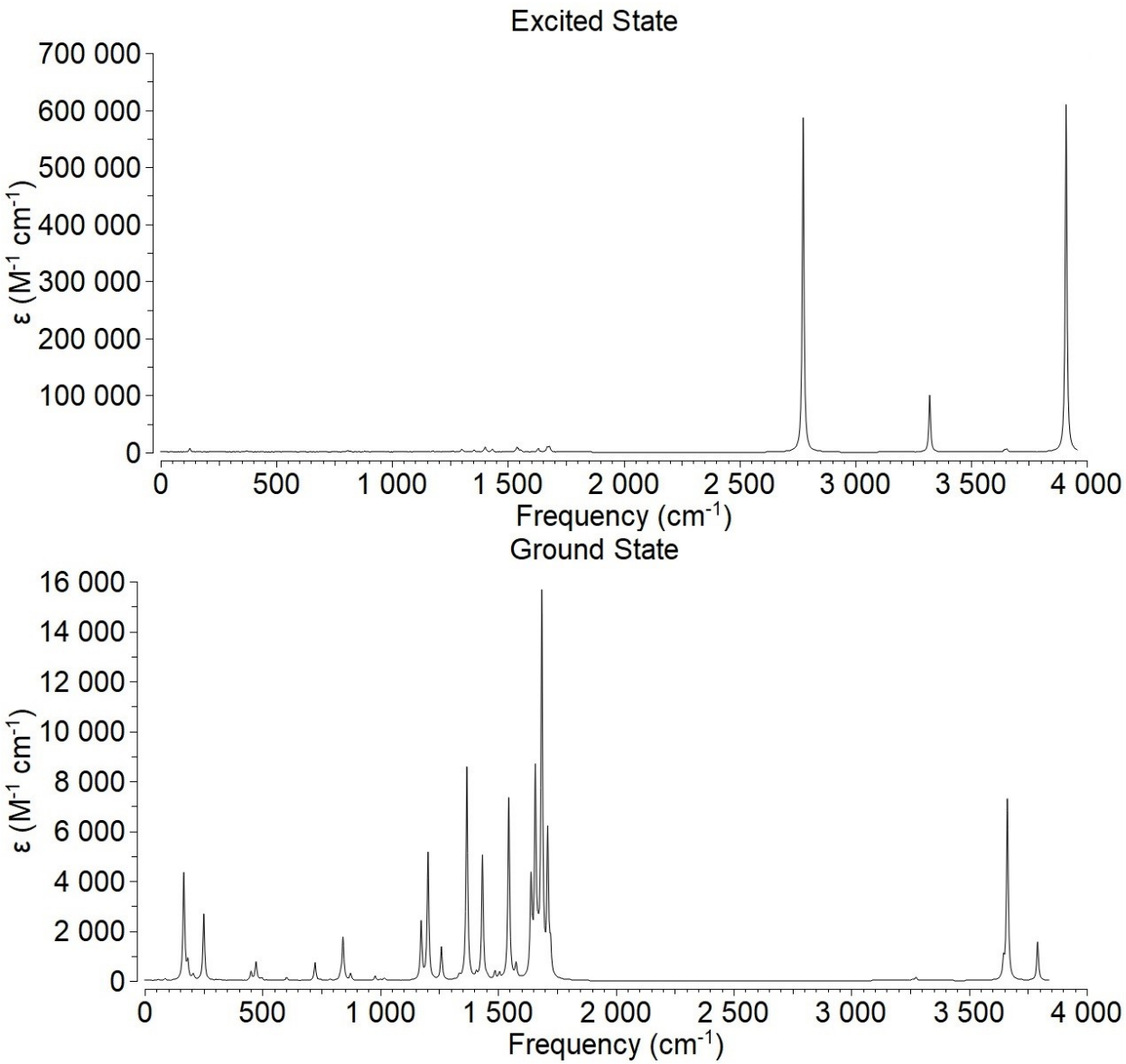

Fig. S96. Calculated vibrational spectra of PF dimer (M052X functional)

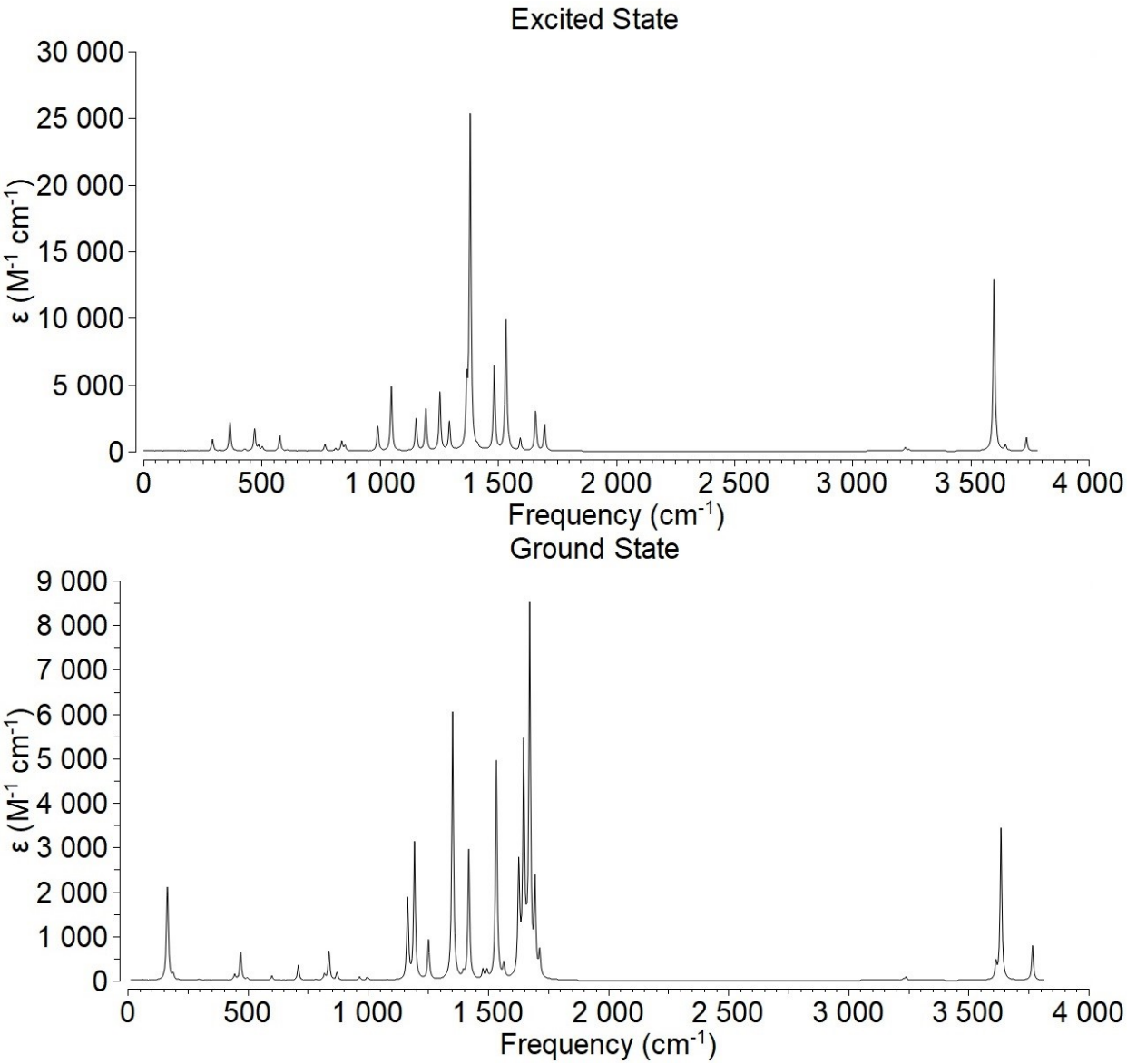

Fig. S97. Calculated vibrational spectra of PF monomer (M062X functional)

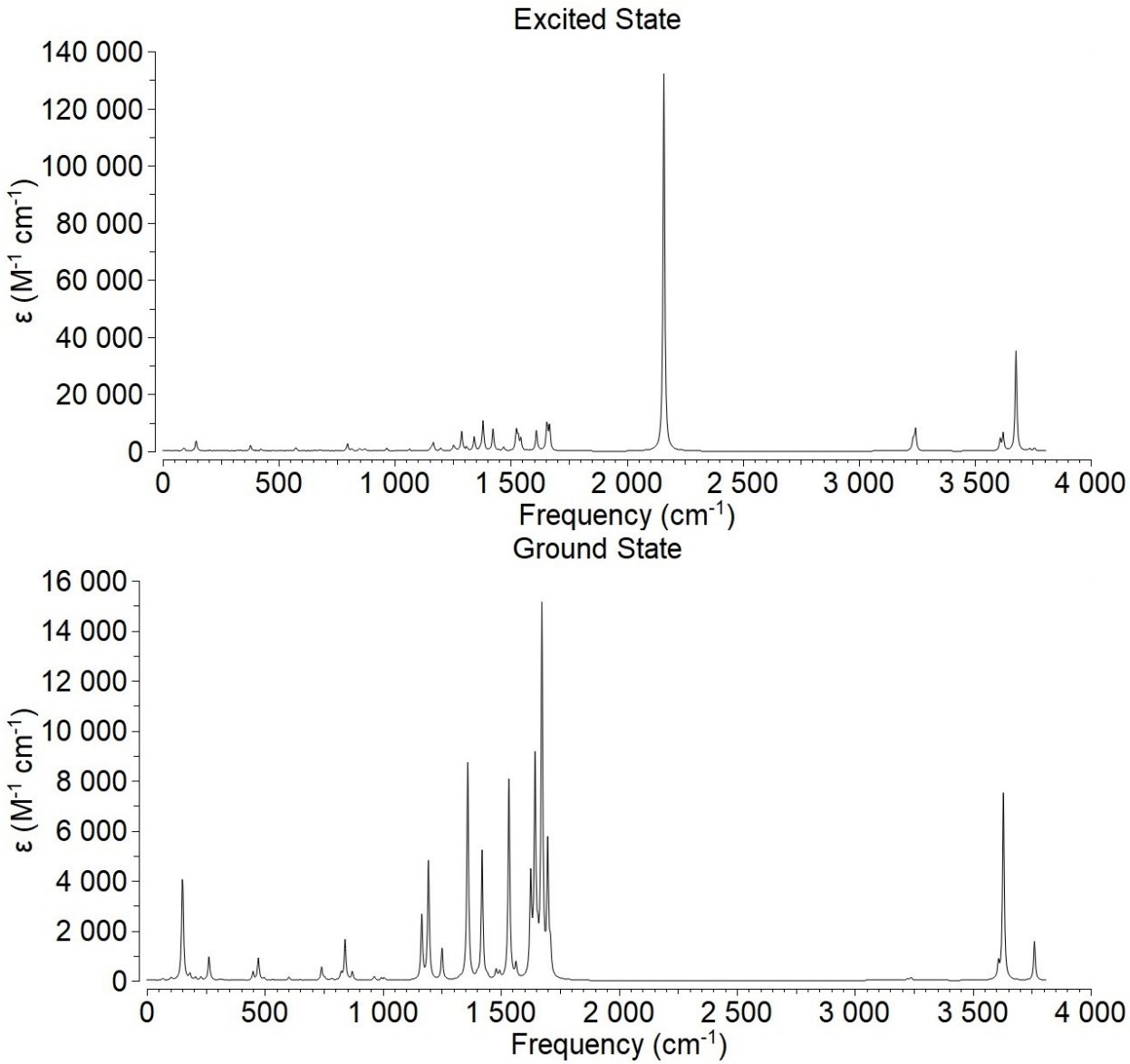

Fig. S98. Calculated vibrational spectra of PF dimer (M062X functional)

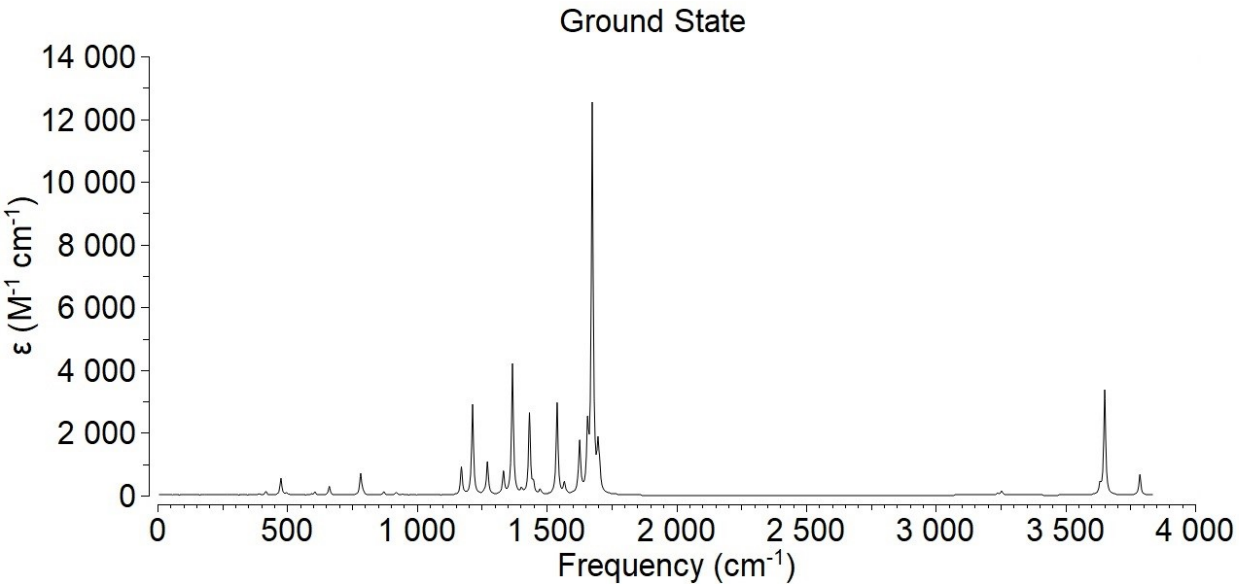

Fig. S99. Calculated vibrational spectra of PF monomer (mPW2PLYP functional with GD3 correction)

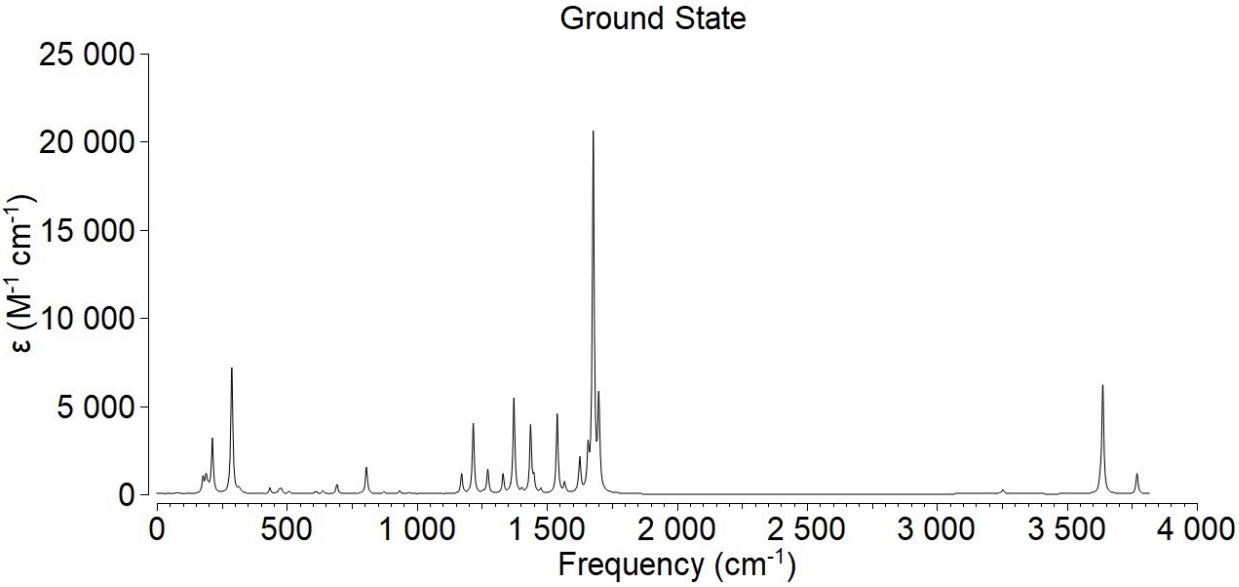

Fig. S100. Calculated vibrational spectra of PF dimer (mPW2PLYP functional with GD3 correction)

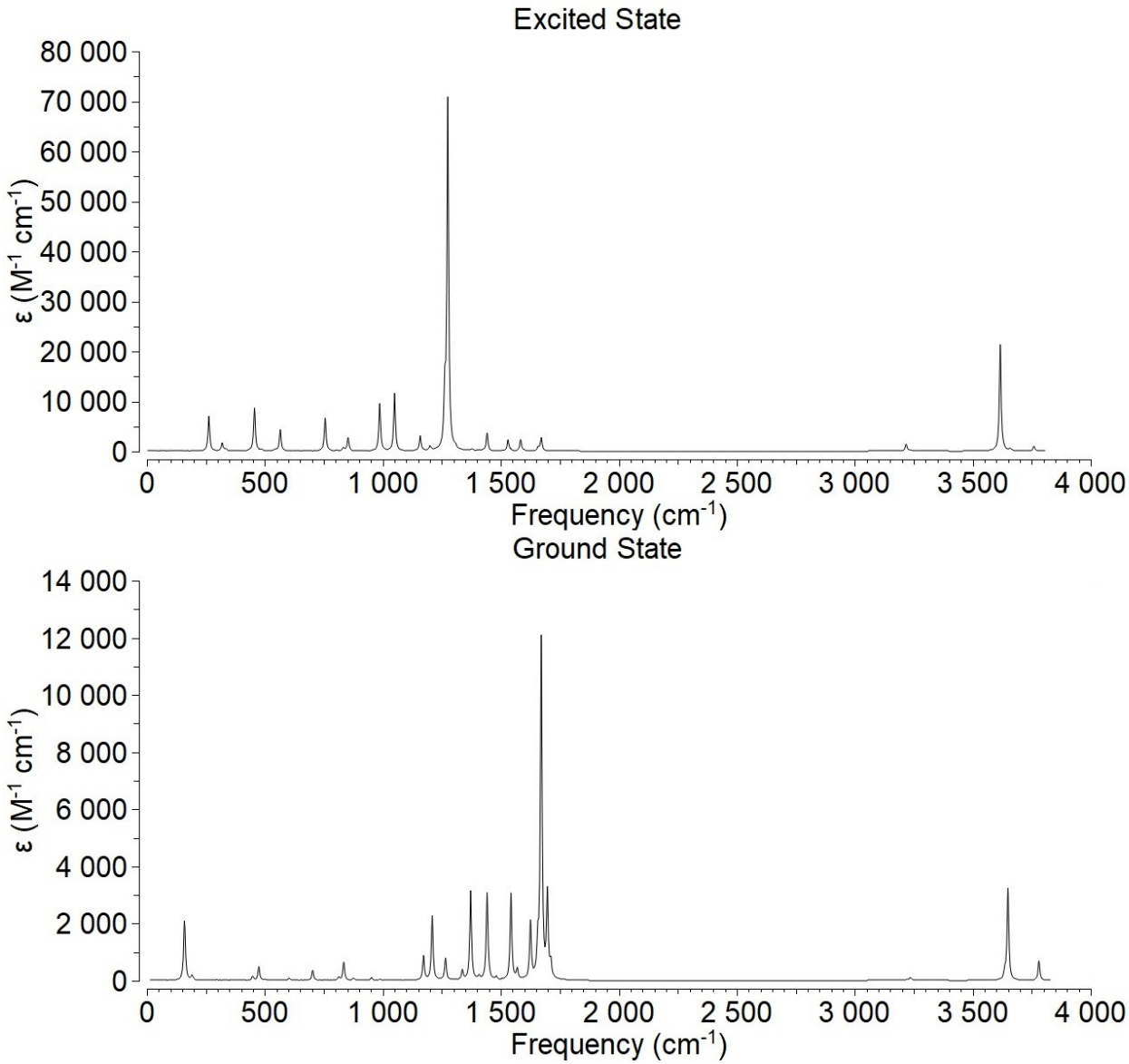

Fig. S101. Calculated vibrational spectra of PF monomer (PBE0 functional with GD3 correction)

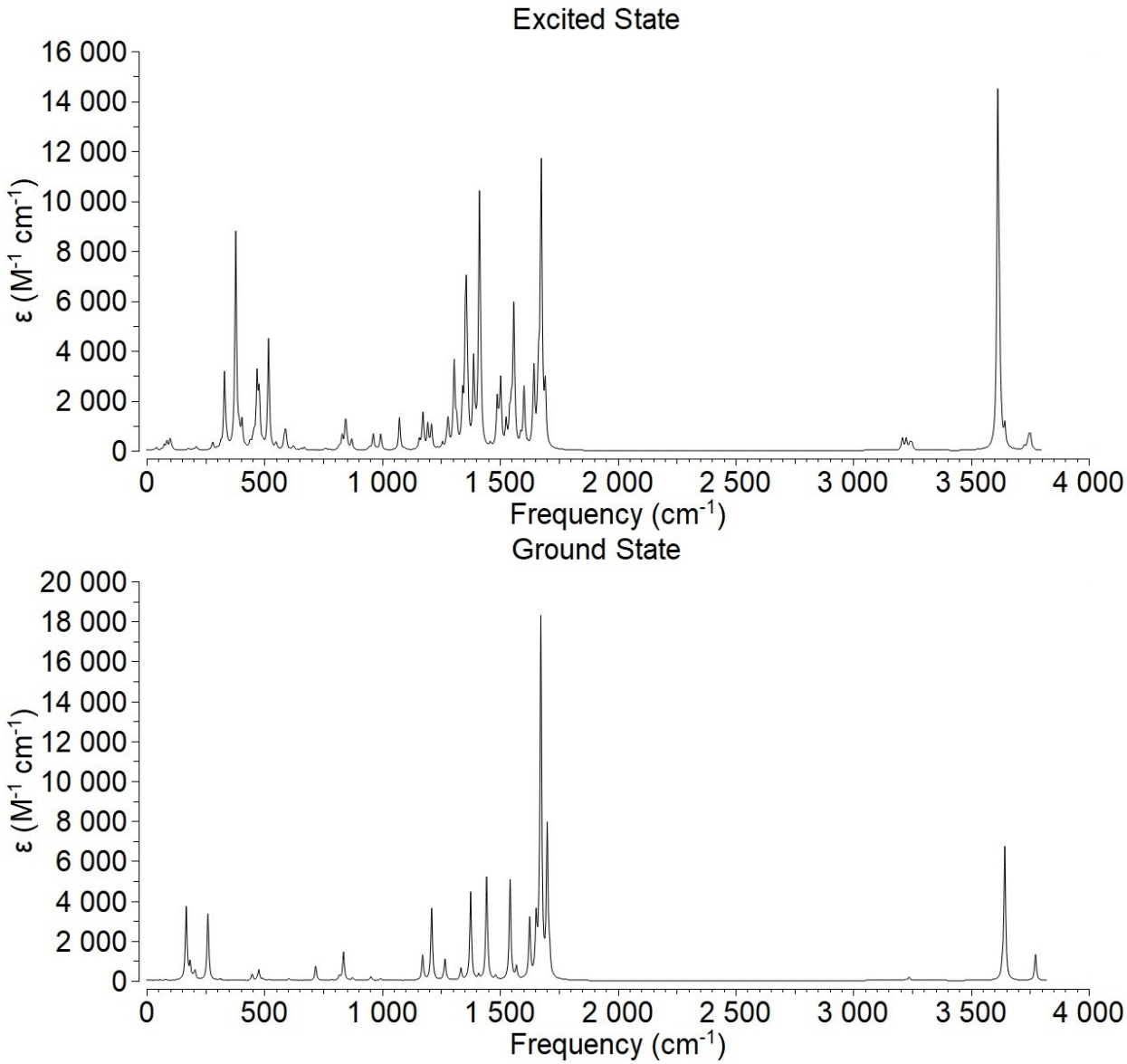

Fig. S102. Calculated vibrational spectra of PF dimer (PBE0 functional with GD3 correction)

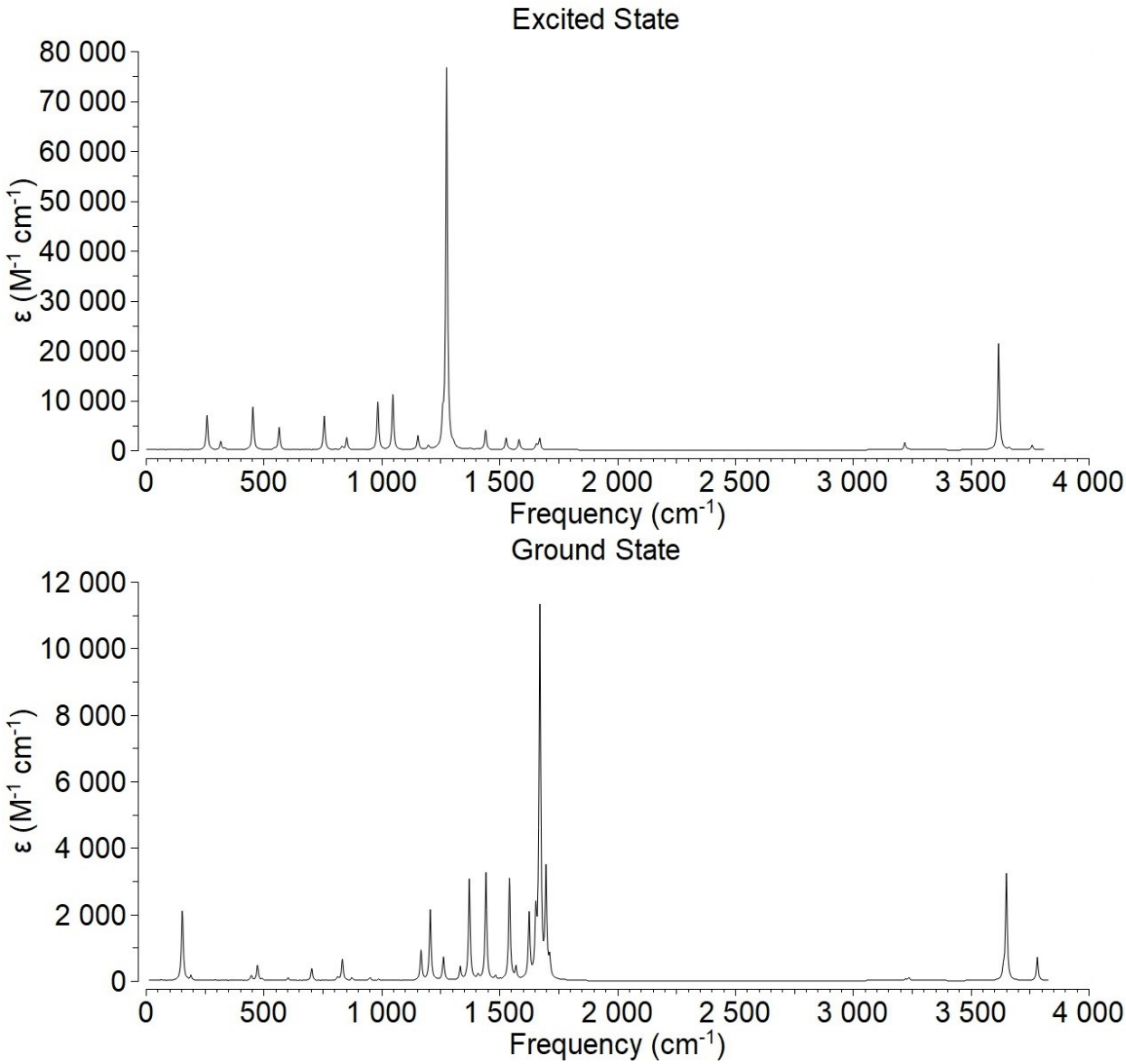

Fig. S103. Calculated vibrational spectra of PF monomer (PBE0 functional with GD3+BJ correction)

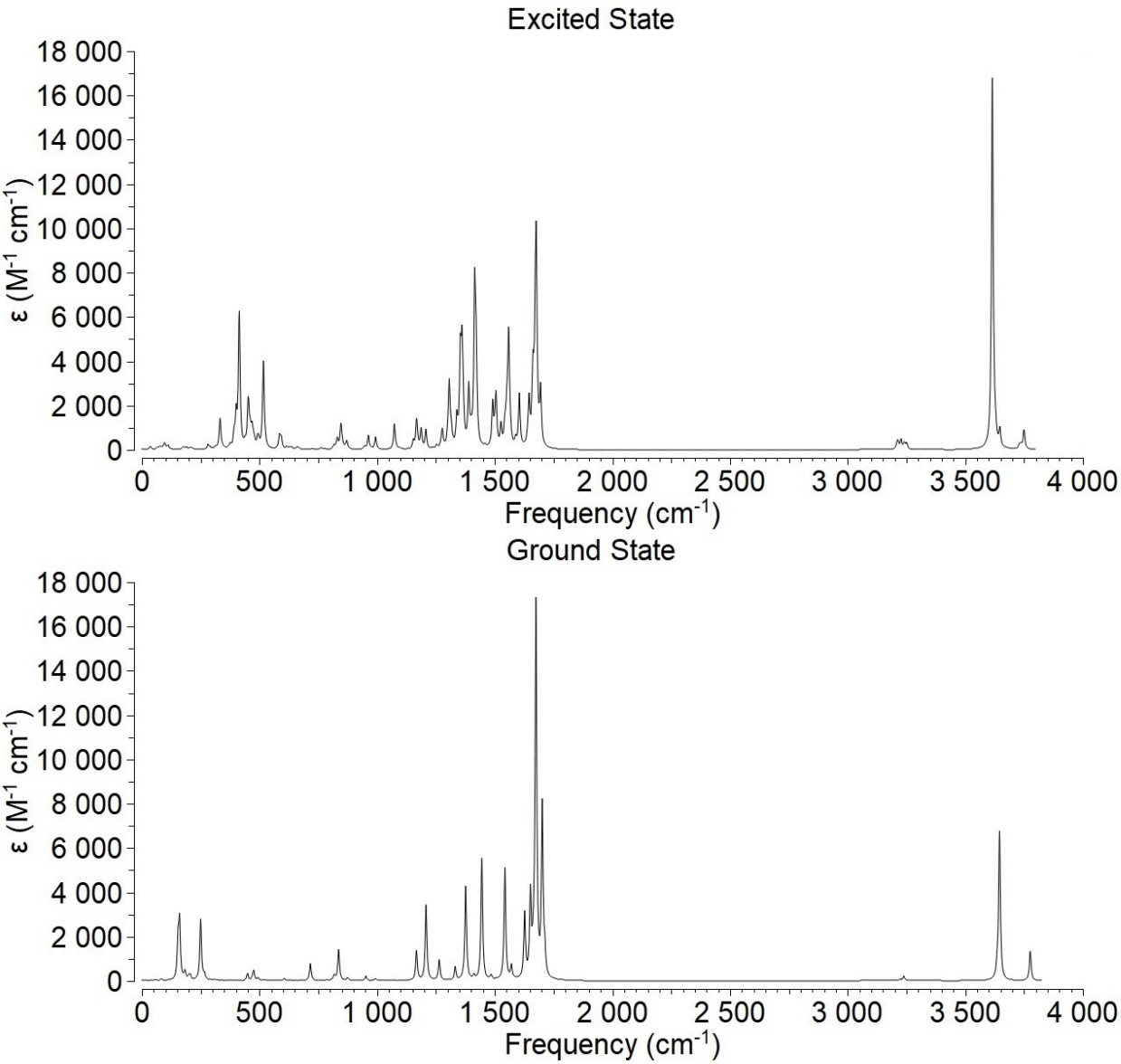

Fig. S104. Calculated vibrational spectra of PF dimer (PBE0 functional with GD3+BJ correction)

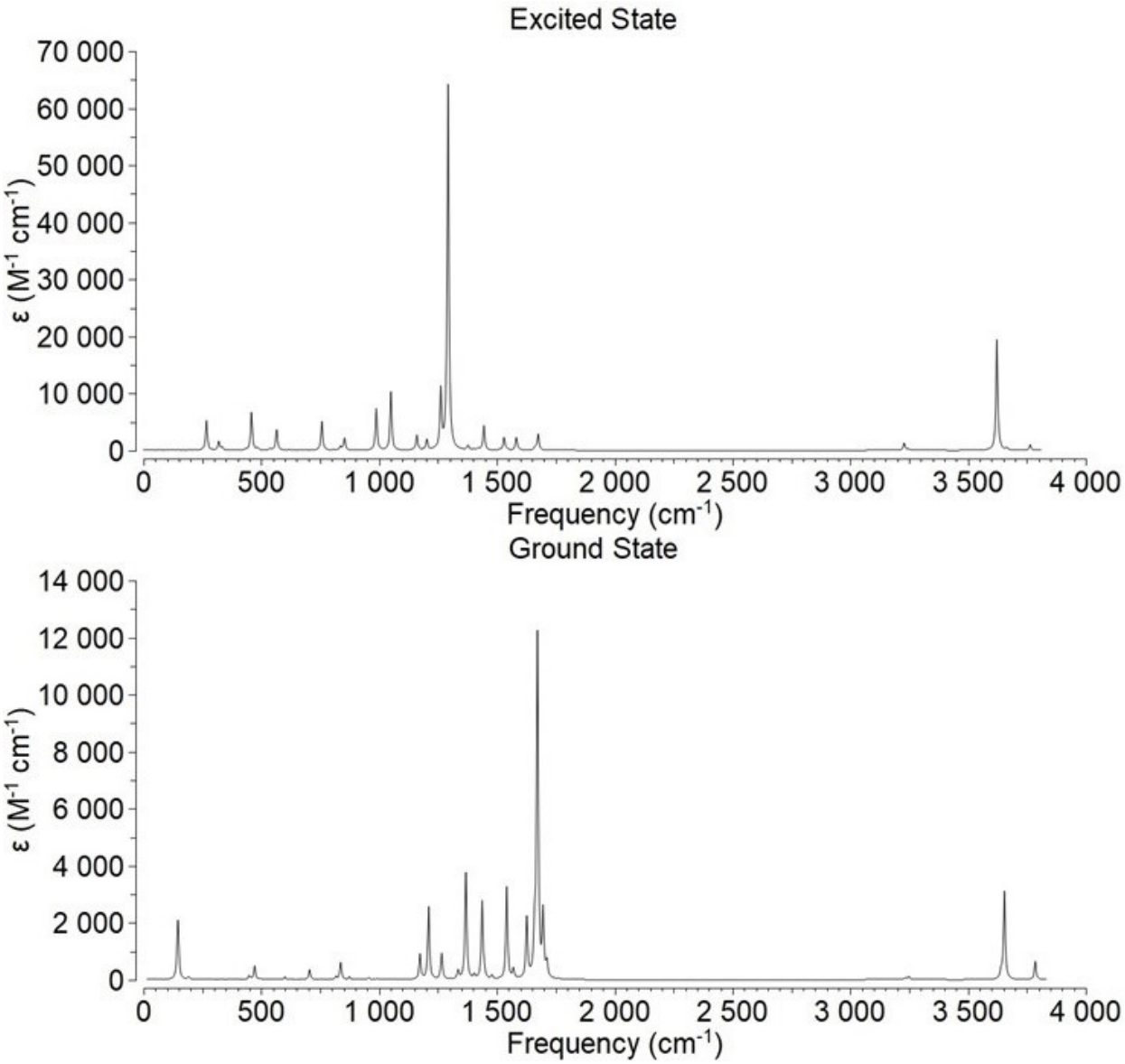

Fig. S105. Calculated vibrational spectra of PF monomer (PW6B95 functional with GD3 correction)

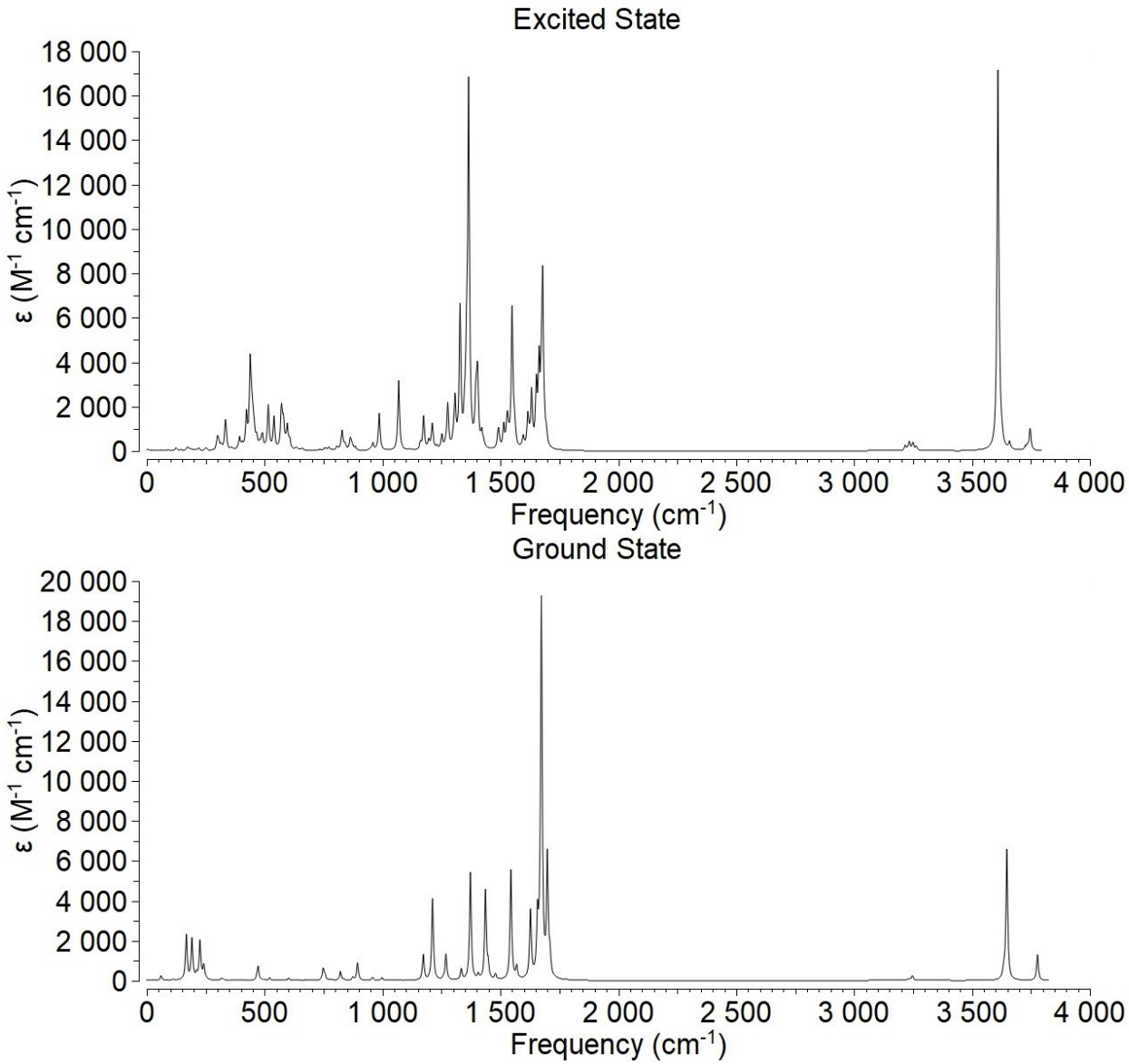

Fig. S106. Calculated vibrational spectra of PF dimer (PW6B95 functional with GD3 correction)

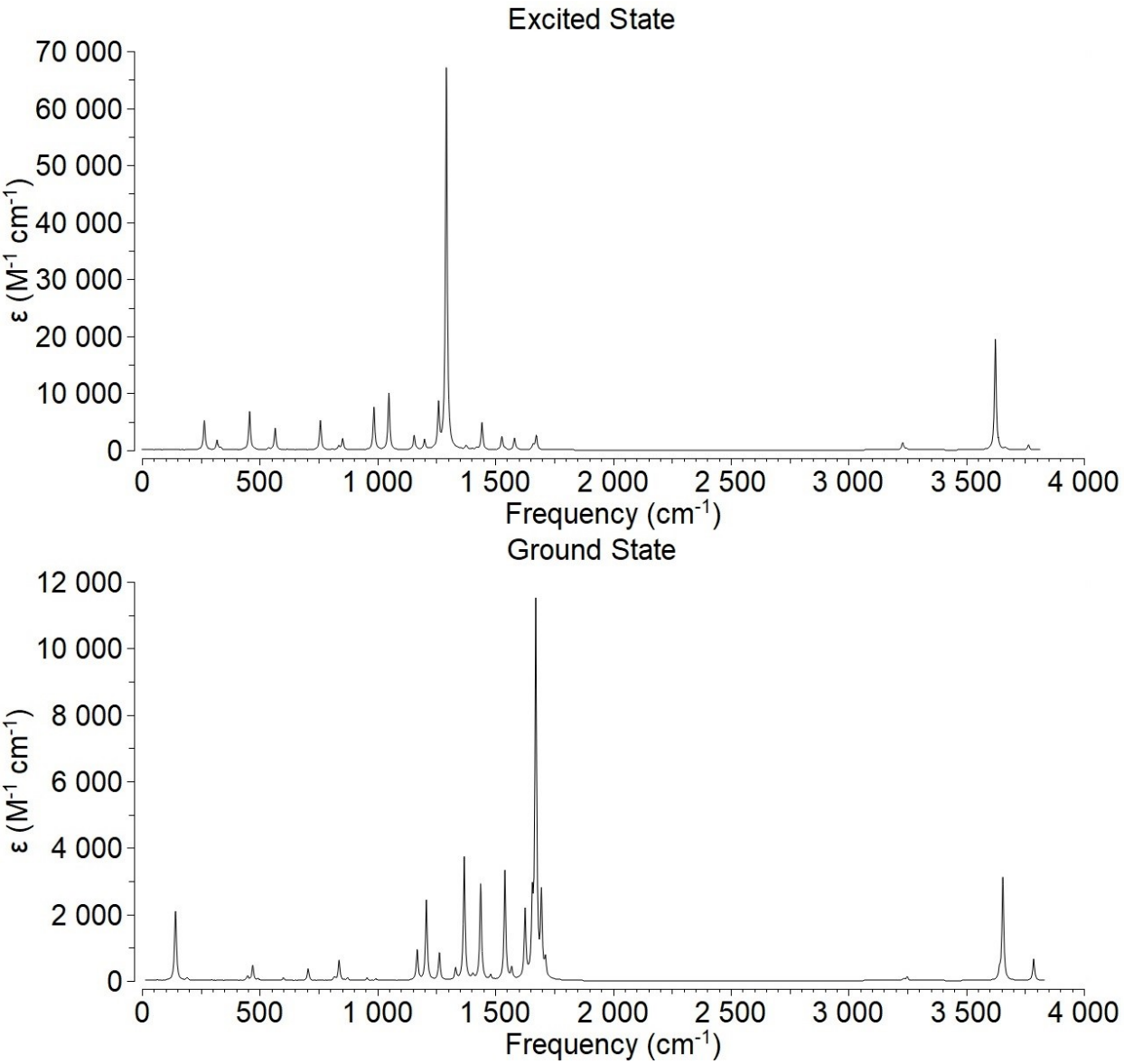

Fig. S107. Calculated vibrational spectra of PF monomer (PW6B95 functional with GD3+BJ correction)

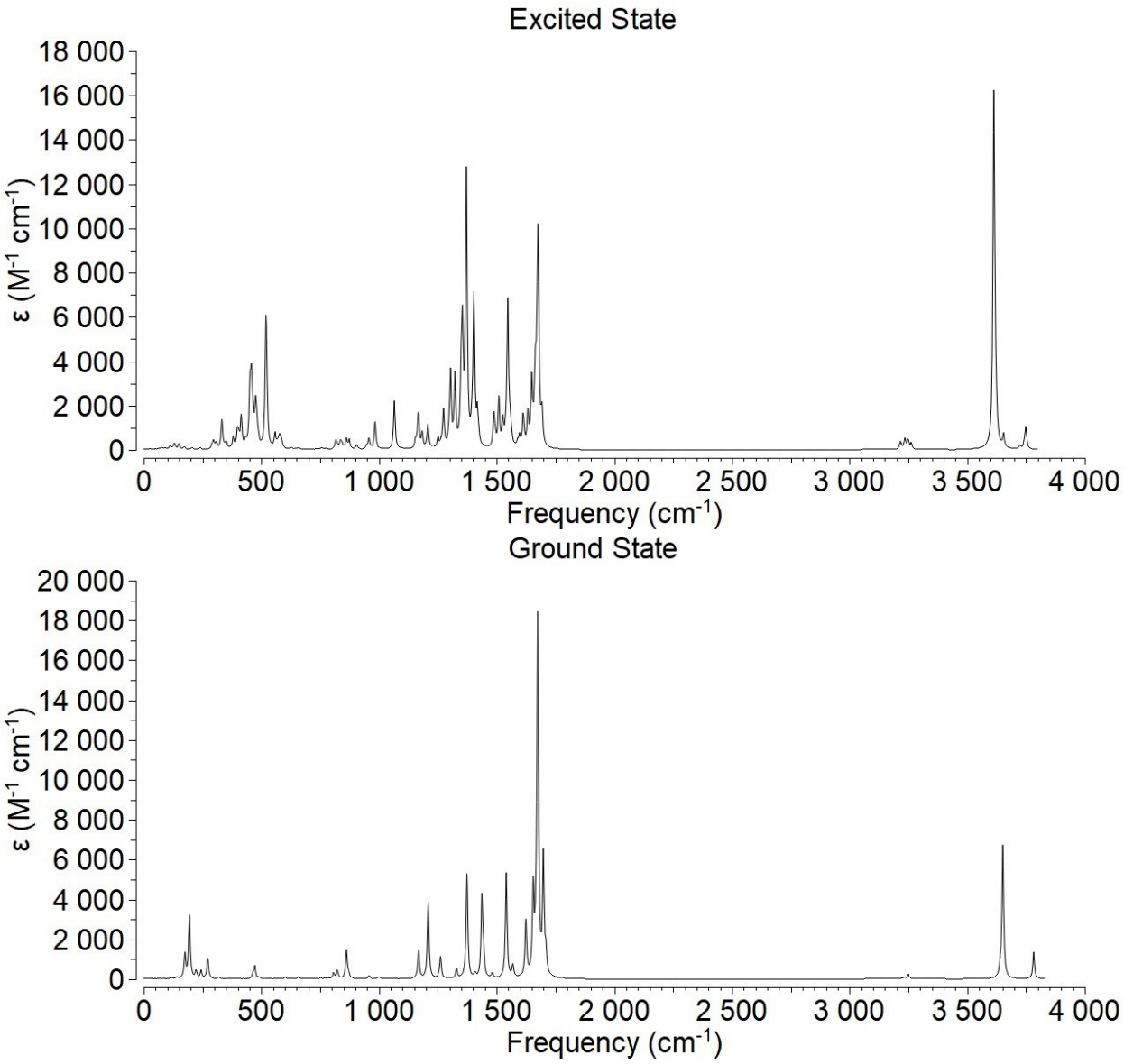

Fig. S108. Calculated vibrational spectra of PF dimer (PW6B95 functional with GD3+BJ correction)

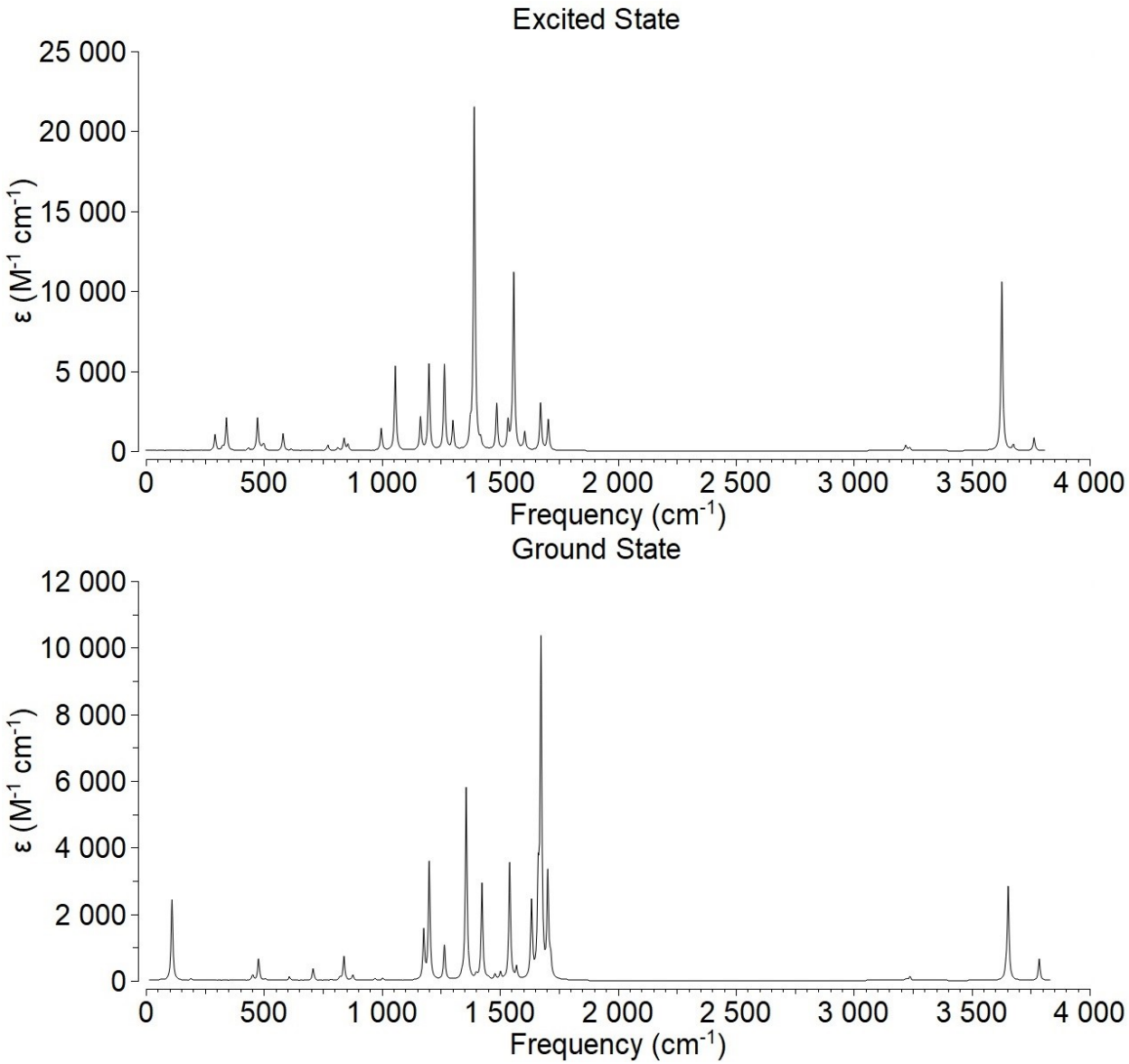

Fig. S109. Calculated vibrational spectra of PF monomer (ωB97XD functional)

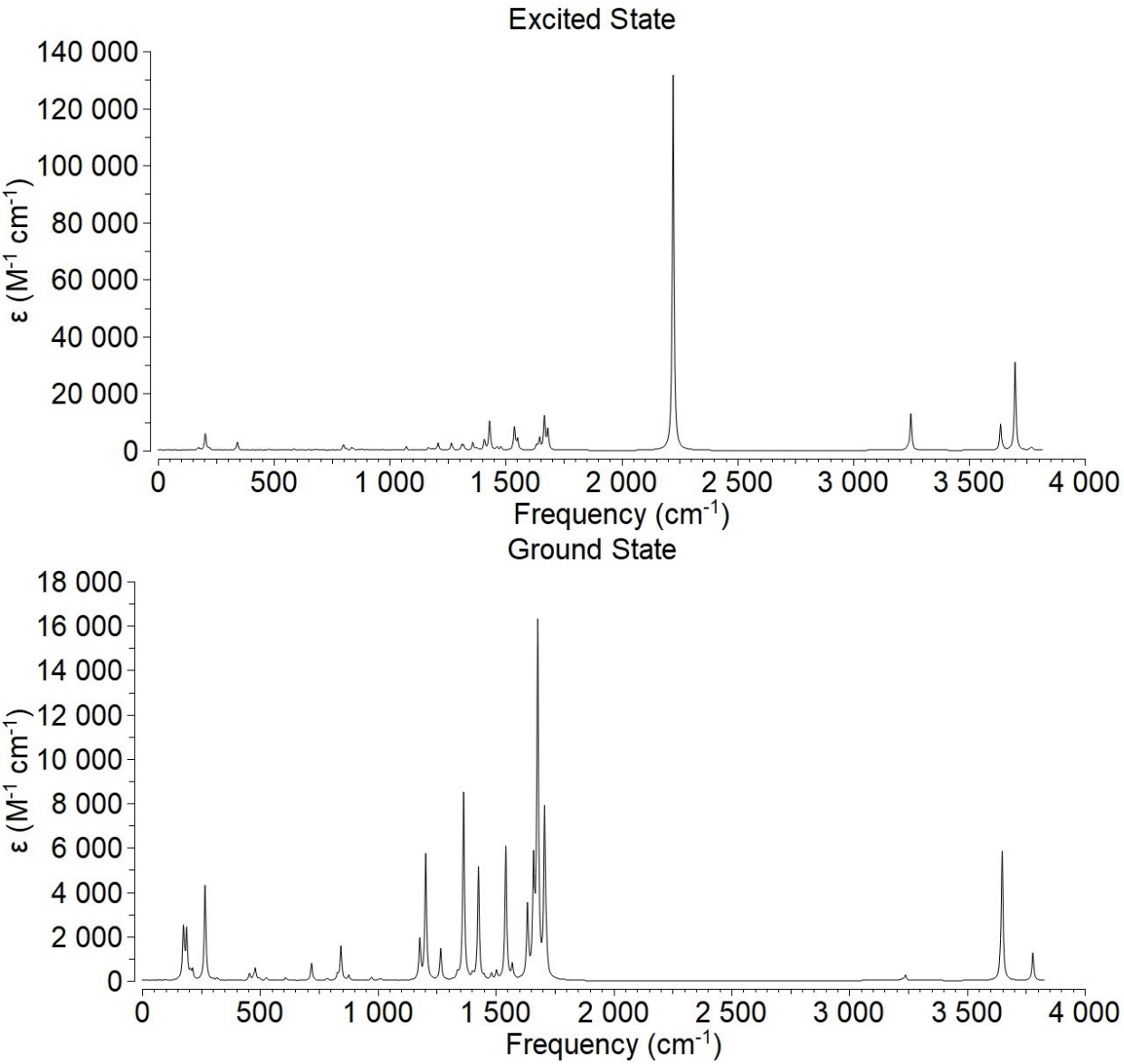

Fig. S110. Calculated vibrational spectra of PF dimer (ωB97XD functional)

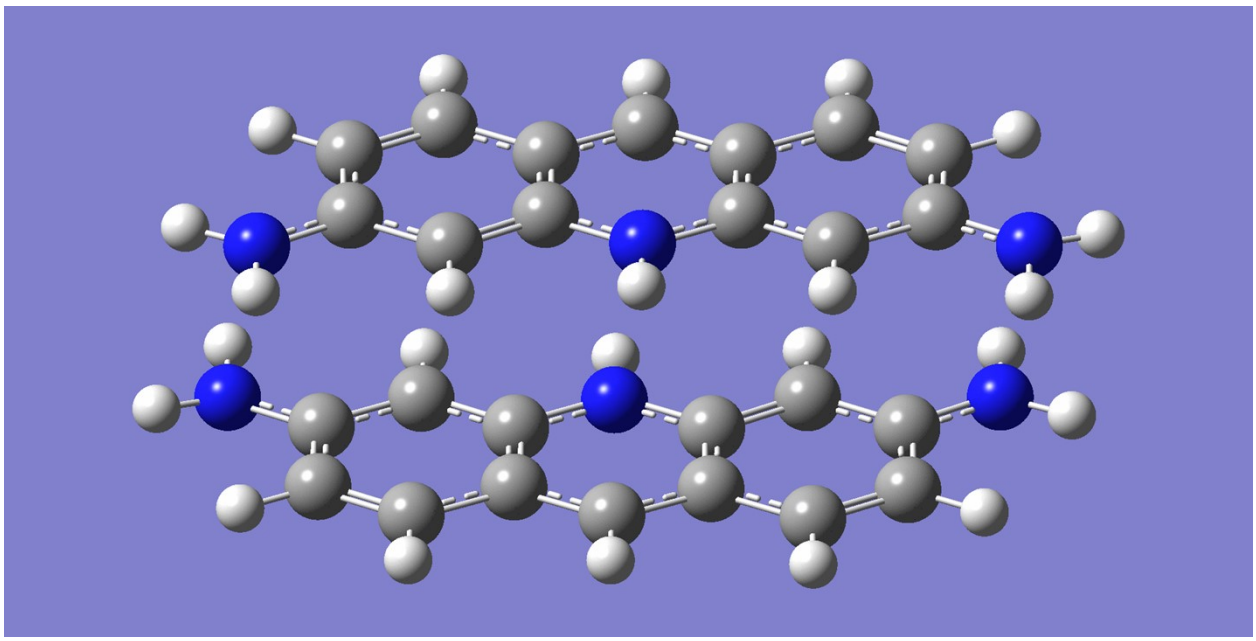

Fig. S111. GIF of vibration #138 in PF dimer (M06HF functional, S_2 excited state)

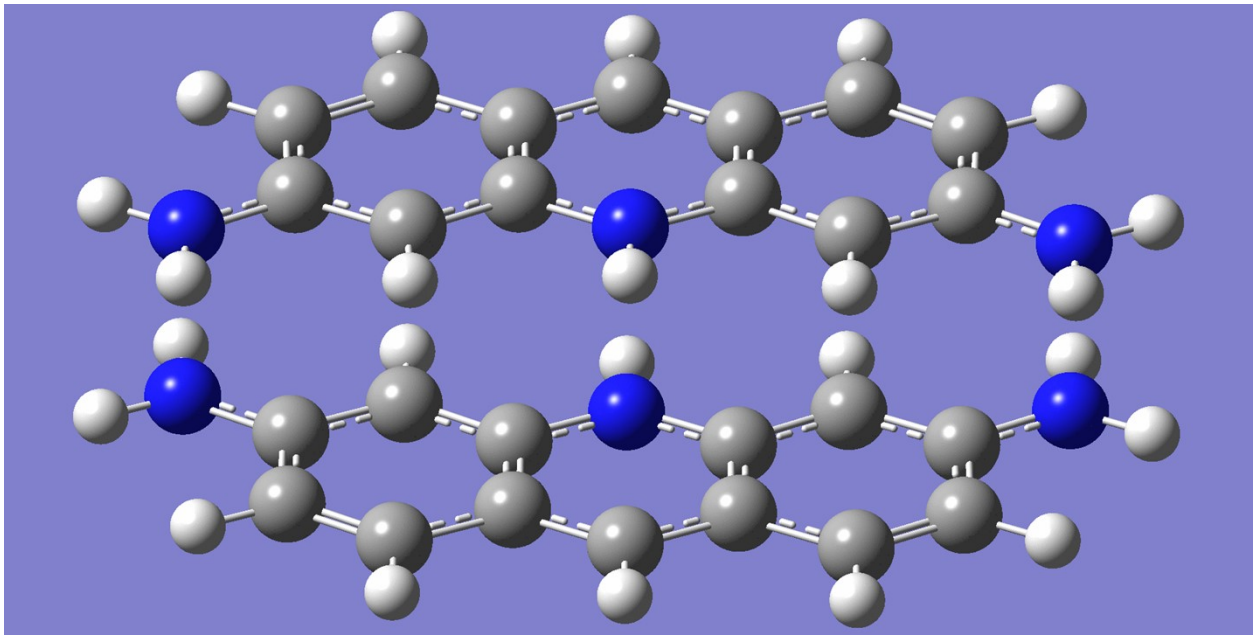

Fig. S112. GIF of vibration #138 in PF dimer (M06HF functional, ground state)

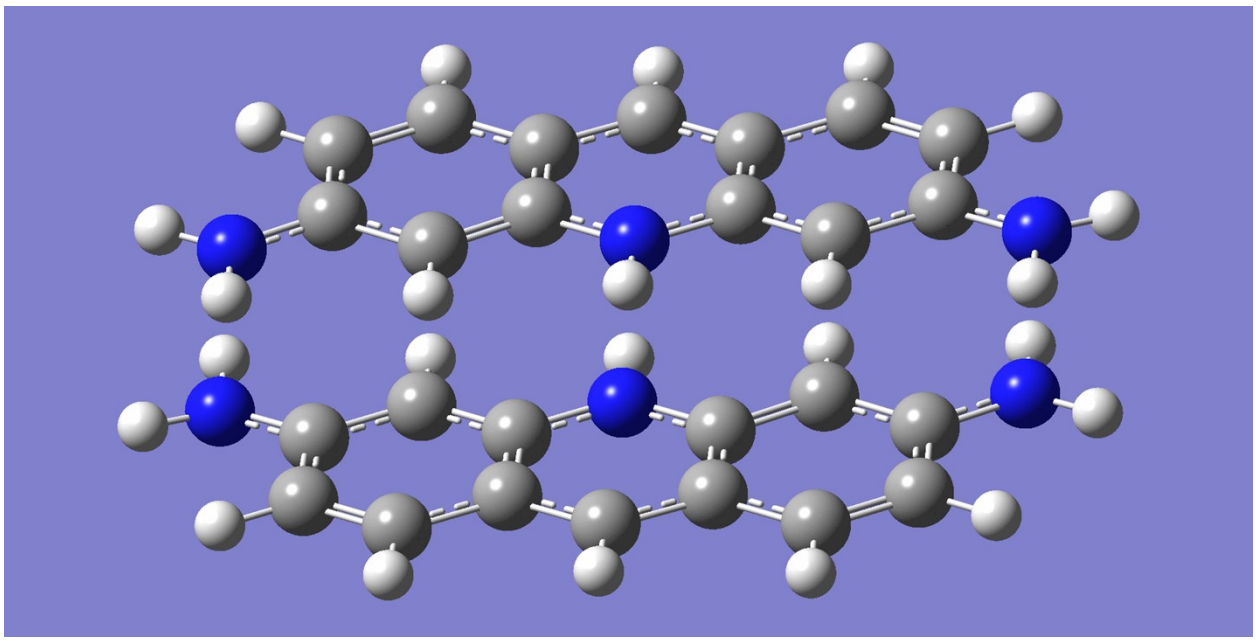

Fig. S113. GIF of vibration #162 in PF dimer (M06HF functional, S_2 excited state)

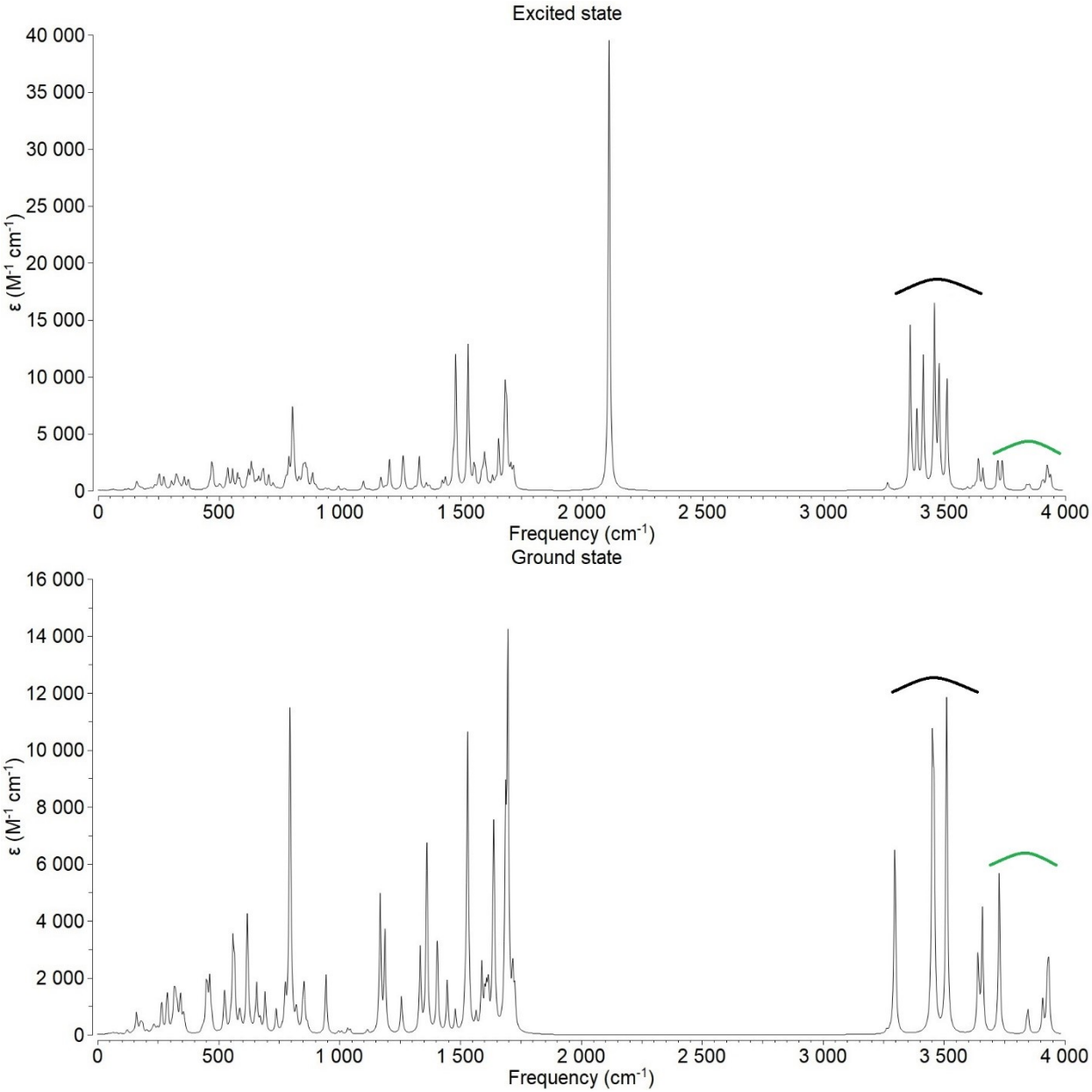

Fig. S114. Calculated vibrational spectra of "PF_2+10H_2O" hydrating complex (M06HF functional). The vibrations of the hydrogen atoms of the imino and amino groups of the proflavine molecules are shown in black arcs, and the vibrations of water molecules in green

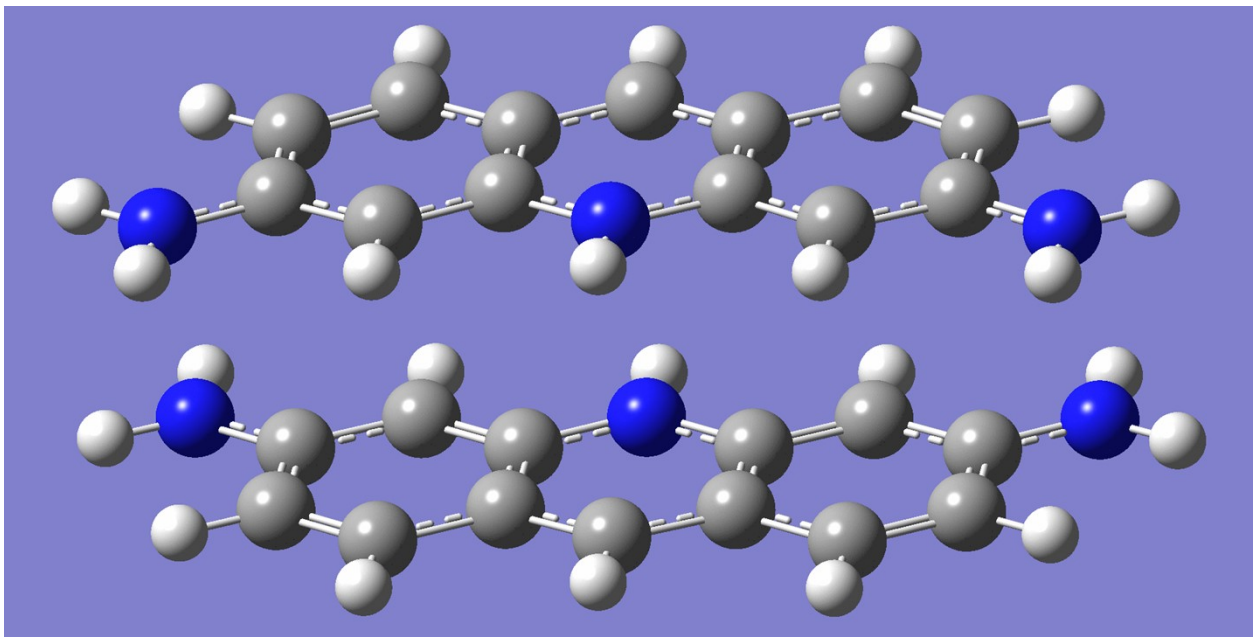

Fig. S115. GIF of vibration #111 in PF dimer (M06HF functional, S_1 excited state)