Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

The Effects of Extended Conjugation Length of Purely Organic Phosphors on Their Phosphorescence Emission Properties

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Supporting Figures

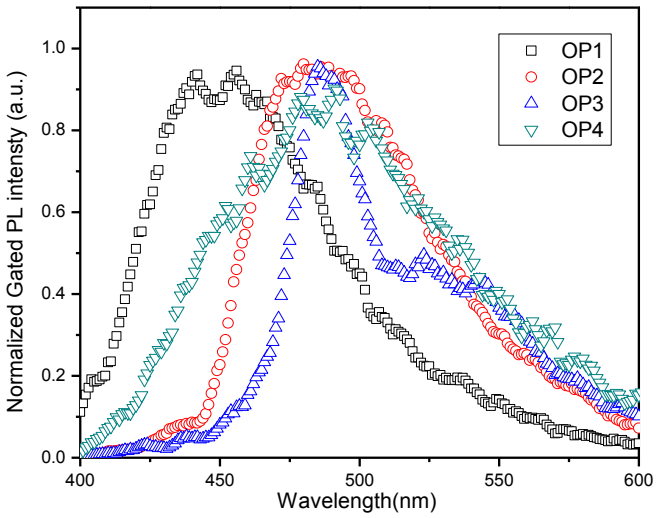

Fig. S1 Time gated photoluminescence spectra at 77K of OP molecules. The excitation wavelength is 320nm.

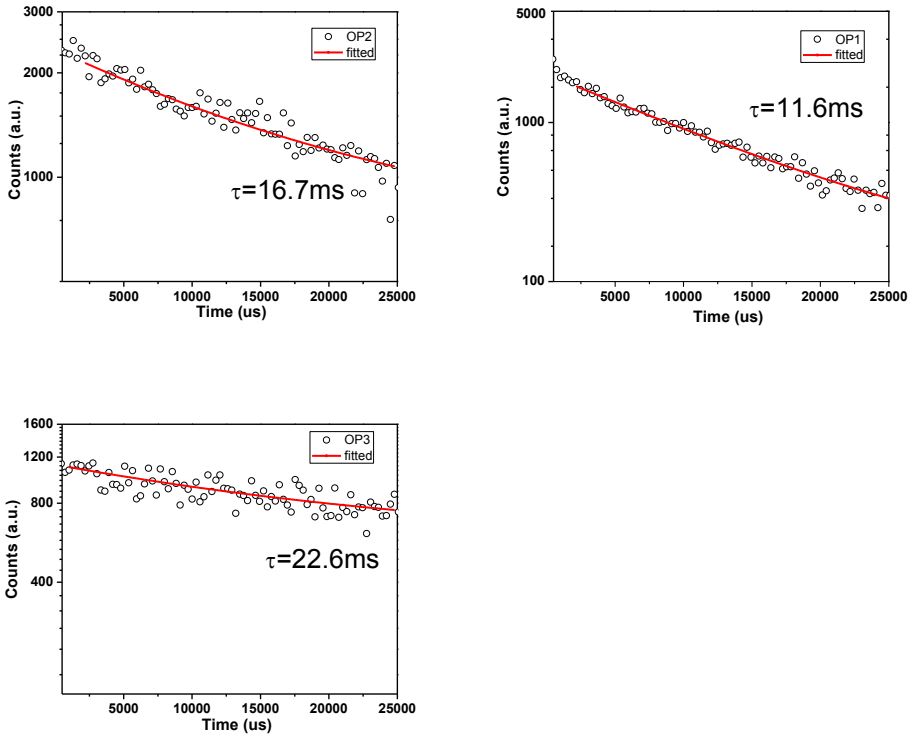

Fig. S2 Time-resolved phosphorescence decay curve for OP1-OP3 and phosphorescence lifetime obtained from curve-fitting. Due to low intensity, phosphorescence lifetime of OP4 cannot be conducted.

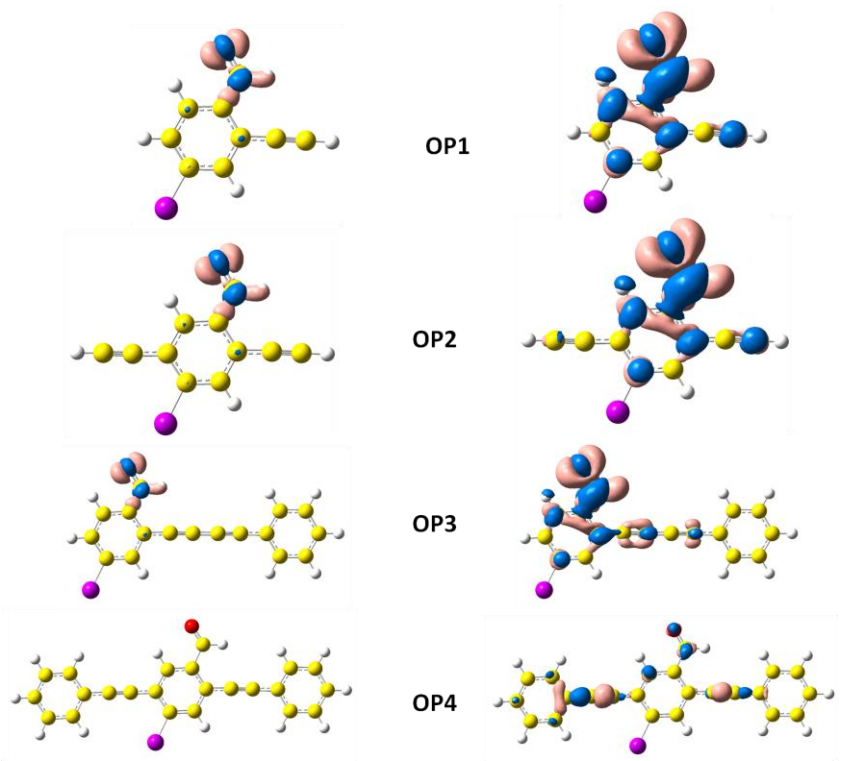

Fig. S3 Plot of the total electron density difference between ground state and excited states, isovalue is in the unit of electrons/Å^3. $S_0 \rightarrow T_2$, left: isovalue = 0.01, right: isovalue = 0.002

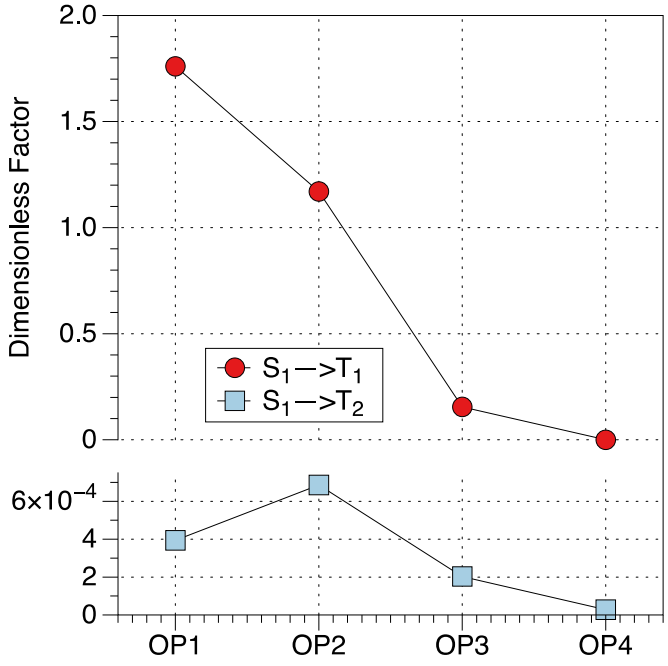

Fig. S4 The dimensionless factor (*10^{-5}) contributing to ISC rate constants according to equation (1).

Calculation of the radiative rate constant

To verify the accuracy in the computations of the ISC rate with the displaced-oscillator model, we compare the computed fluorescence rate(k_{fl}). The value is obtained from the following equation (Eq. S1)[S1].

$$K_{rad}(i \rightarrow f) = \frac{4e^2}{3c^3\hbar^4}\Delta E_{i,f}^3 \, u_{el}(i,f)^2 \quad \text{(S1)}$$

$u_{el}(i,f)^2$ is the trasition dipole moment between the initial state i and the final state of f, $\Delta E_{i,f}$ is the vertical energy gap between the two state.

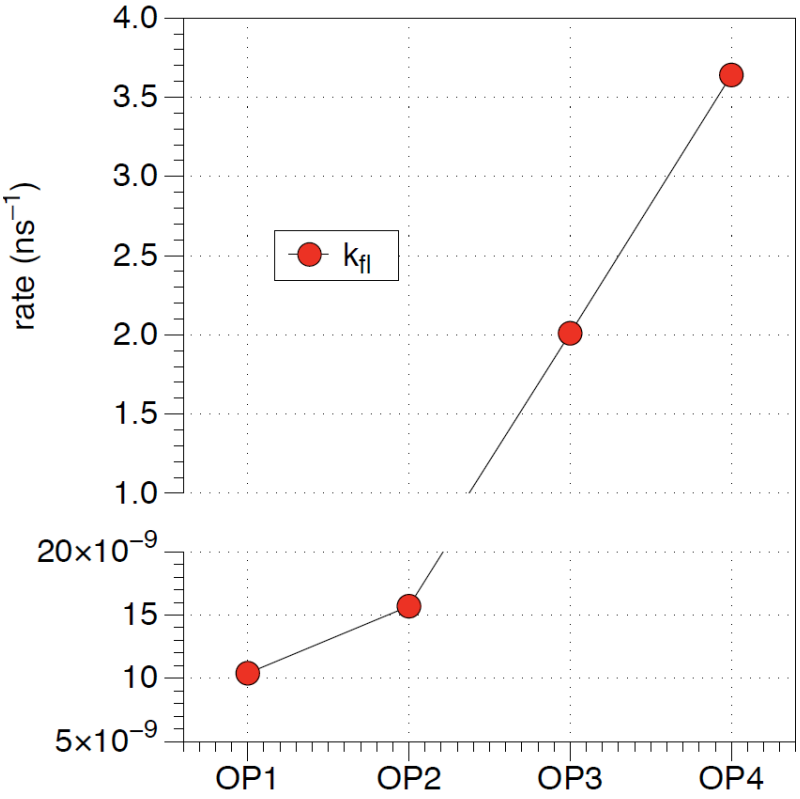

Fig. S5 The rate constants of fluorescence rate for S_1->S_0 calculated according to equation (S1).

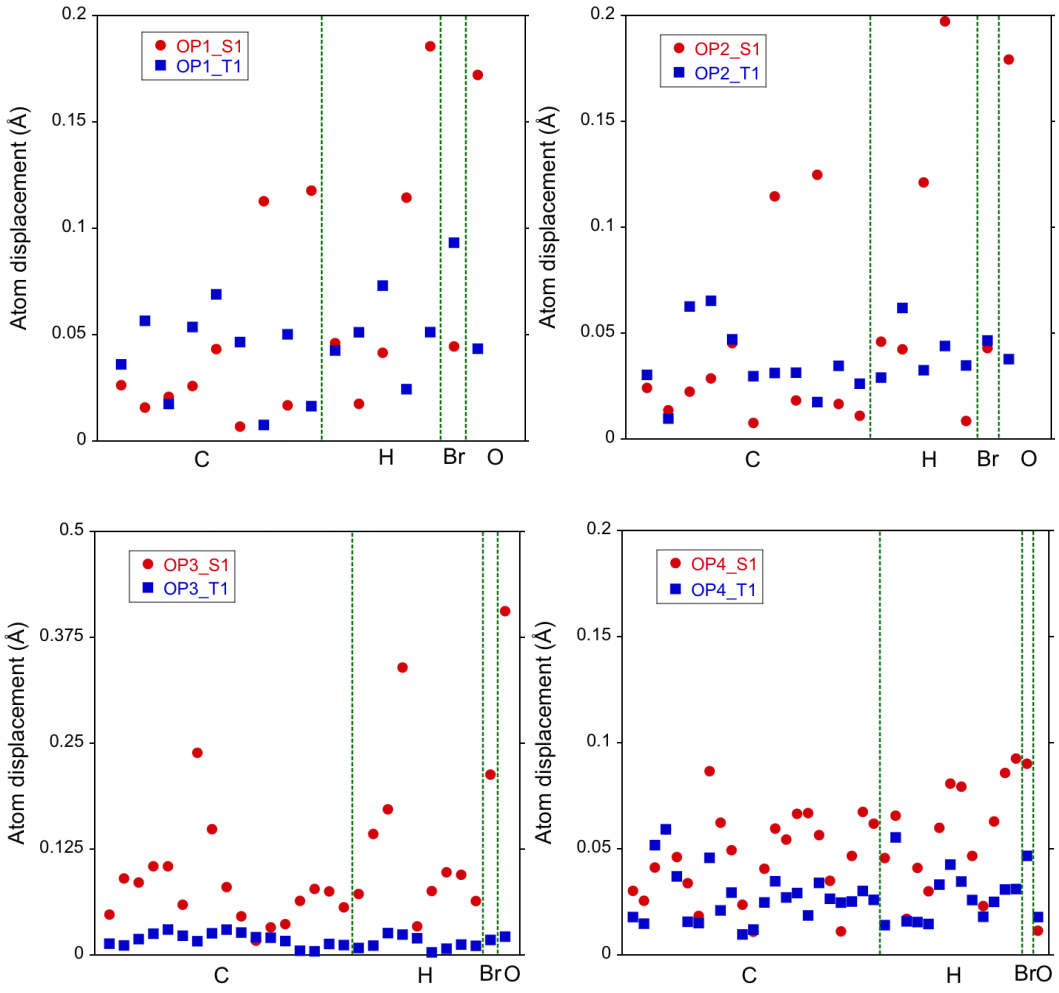

Fig. S6 The atom displacements of OP1-OP4 between excited states (S_1, T_1) and ground state (S_0). The x-axis is divided into four regions, each containing the same atom type.

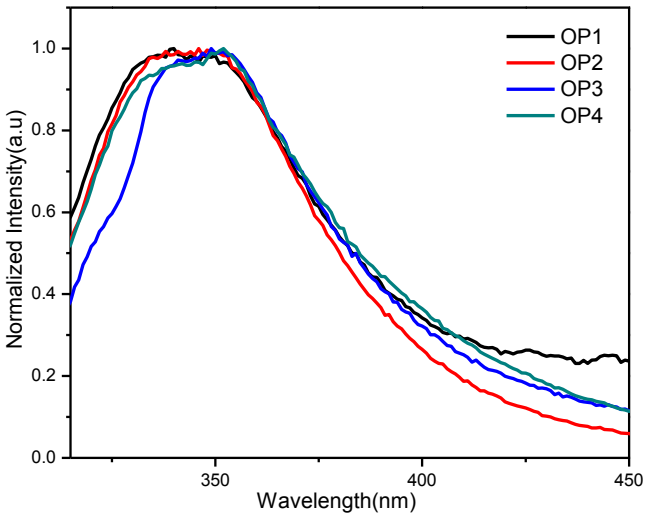

Fig. S7. Normalized fluorescence spectra of OP molecules at room temperature. The excitation wavelength is 300nm.

Table S1 Vibrational frequencies ω and Huang-Rhys factors S for $S_1 \rightarrow T_1$ and $S_1 \rightarrow T_2$ transitions for OP1-OP4

OP1($S_1 \rightarrow T_1$)				OP1($S_1 \rightarrow T_2$)			
S_1		**T_1**		**S_1**		**T_2**	
ω(cm^{-1})	**S**	**ω(cm^{-1})**	**S**	**ω(cm^{-1})**	**S**	**ω(cm^{-1})**	**S**
119	0.363	111	1.479	119	0.355	98	1.294
150	1.721	144	0.056	150	1.734	144	0.004
298	0.216	259	0.019	252	0.001	258	0.026
438	0.168	300	0.039	298	0.218	298	0.027
461	0.073	431	0.030	438	0.166	428	0.060
634	0.067	453	0.106	461	0.073	454	0.117
672	0.002	603	0.117	634	0.069	602	0.107
771	0.470	622	0.067	672	0.002	620	0.091
864	0.019	659	0.003	771	0.471	723	0.346
1079	0.071	725	0.406	864	0.020	872	0.008
1111	0.041	871	0.008	1079	0.071	993	0.094
1169	0.002	996	0.092	1111	0.040	1088	0.121
1212	0.227	1076	0.170	1169	0.002	1154	0.031
1232	0.172	1142	0.024	1212	0.226	1194	0.036
1289	0.014	1197	0.015	1232	0.168	1211	0.080
1422	0.139	1214	0.104	1289	0.014	1251	0.021
1450	0.280	1252	0.037	1422	0.138	1304	0.058
1504	0.075	1305	0.070	1450	0.276	1405	0.001
1562	0.160	1399	0.032	1504	0.074	1455	0.293
1611	0.008	1433	0.337	1562	0.156	1475	0.064
2172	0.066	1477	0.047	1611	0.007	1545	0.108
2904	0.003	1528	0.055	2172	0.065	1630	0.006
3485	0.001	2091	0.060	2904	0.002	2103	0.071

		2971	0.001	3485	0.001	2987	0.001
		3477	0.001			3477	0.001
OP2($S_1 \rightarrow T_1$)				OP2($S_1 \rightarrow T_2$)			
S_1		**T_1**		**S_1**		**T_2**	
ω(cm^{-1})	**S**	**ω(cm^{-1})**	**S**	**ω(cm^{-1})**	**S**	**ω(cm^{-1})**	**S**
52	0.073	33	0.003	52	0.064	70	0.138
100	0.170	93	3.223	100	0.147	139	0.198
118	0.452	118	0.001	118	0.448	142	1.450
119	0.255	121	0.212	119	0.256	150	0.110
149	0.933	126	0.045	149	0.936	186	1.145
167	0.147	161	1.146	167	0.129	247	0.615
226	0.033	165	0.005	226	0.028	304	0.002
247	0.202	211	0.001	247	0.204	327	0.563
291	0.396	245	0.198	291	0.398	394	0.037
308	0.061	270	0.555	308	0.051	410	0.983
376	0.249	287	0.442	376	0.203	426	0.027
389	0.152	335	0.712	389	0.151	456	0.001
440	0.025	382	0.129	440	0.025	502	0.041
505	0.076	432	0.024	505	0.239	516	0.041
522	0.010	434	0.010	522	0.011	561	0.003
526	0.088	444	0.010	526	0.013	576	0.022
594	0.043	554	0.035	594	0.043	583	0.349
597	0.001	572	0.537	597	0.001	627	0.293
647	0.044	588	0.080	647	0.021	654	1.350
648	0.057	616	0.003	648	0.057	659	0.416
672	0.052	630	0.016	672	0.051	674	0.114
690	0.168	647	0.211	690	0.168	724	0.087
716	0.001	660	0.122	785	0.001	756	0.086
785	0.001	672	0.235	788	0.218	906	0.004
788	0.218	802	0.237	996	0.029	914	0.028
925	0.001	884	0.007	1130	0.075	937	0.056
996	0.029	930	0.004	1176	0.012	1055	0.003
1130	0.075	946	0.043	1206	0.038	1101	0.314
1176	0.012	1070	0.031	1236	0.447	1132	0.013
1206	0.038	1082	0.420	1275	0.270	1239	0.172
1236	0.448	1208	0.024	1339	0.023	1250	0.004
1275	0.269	1264	0.153	1380	0.042	1295	0.162
1339	0.023	1305	0.093	1441	0.458	1368	0.020
1380	0.042	1369	0.001	1495	0.010	1425	0.075
1441	0.462	1437	0.260	1557	0.231	1510	0.138
1495	0.010	1481	0.554	1590	0.858	1562	1.007
1557	0.232	1543	0.265	2168	0.059	1656	0.067
1590	0.854	1731	0.197	2227	0.098	2085	0.027
2168	0.059	1857	0.024	2898	0.003	2159	0.099
2227	0.097	2003	0.104	3485	0.001	2930	0.001
2898	0.003	2970	0.003	3490	0.002	3205	0.001
3485	0.001	3475	0.001			3480	0.001
3490	0.002						
OP3($S_1 \rightarrow T_1$)				OP3($S_1 \rightarrow T_2$)			
S_1		**T_1**		**S_1**		**T_2**	
ω(cm^{-1})	**S**	**ω(cm^{-1})**	**S**	**ω(cm^{-1})**	**S**	**ω(cm^{-1})**	**S**
21	1.616	20	1.514	21	0.070	21	0.070

66	0.809	60	0.622	66	0.037	66	0.036
127	0.972	136	1.064	127	0.112	128	0.108
183	0.422	179	0.473	183	0.040	184	0.040
227	0.232	232	0.106	227	0.005	225	0.002
269	0.044	263	0.067	269	0.001	268	0.002
293	0.224	298	0.915	293	0.068	298	0.076
413	0.021	415	0.006	413	0.001	416	0.006
471	0.075	472	0.047	471	0.012	470	0.011
500	0.007	480	0.004	632	0.004	631	0.008
636	0.013	546	0.003	636	0.020	636	0.014
653	0.019	599	0.078	682	0.007	684	0.006
682	0.041	644	0.005	776	0.002	778	0.004
845	0.005	691	0.106	1002	0.007	1003	0.003
1002	0.072	790	0.100	1009	0.001	1086	0.003
1009	0.073	847	0.244	1052	0.013	1118	0.024
1052	0.106	963	0.040	1058	0.021	1172	0.010
1058	0.248	1004	0.013	1073	0.004	1205	0.001
1073	0.012	1102	0.063	1167	0.001	1211	0.047
1167	0.055	1151	0.021	1219	0.021	1228	0.001
1206	0.022	1187	0.066	1298	0.010	1291	0.005
1219	0.073	1220	0.029	1339	0.003	1326	0.002
1234	0.144	1277	0.215	1381	0.004	1379	0.004
1298	0.002	1331	0.041	1385	0.010	1425	0.025
1339	0.004	1350	0.015	1507	0.001	1457	0.007
1381	0.413	1402	0.047	1603	0.004	1519	0.002
1385	0.227	1448	0.179	2097	0.002	1530	0.013
1457	0.003	1472	0.019	2810	0.005	1537	0.001
1500	0.017	1512	0.026			2200	0.006
1507	0.276	1539	0.017			2258	0.006
1536	0.004	1544	0.064			3023	0.002
1603	0.009	1584	0.061				
1647	0.023	1735	0.004				
2097	0.048	1881	0.008				
2189	0.071	2021	0.439				
2810	0.045	2958	0.001				
OP4($S_1 \rightarrow T_1$)				OP4($S_1 \rightarrow T_2$)			
S_1		**T_1**		**S_1**		**T_2**	
ω(cm^{-1})	**S**	**ω(cm^{-1})**	**S**	**ω(cm^{-1})**	**S**	**ω(cm^{-1})**	**S**
16	0.029	18	0.026	16	0.028	17	0.047
32	0.143	33	0.159	32	0.434	33	0.410
106	0.004	107	0.005	106	0.074	106	0.065
111	0.001	111	0.001	111	0.062	112	0.052
142	0.035	142	0.038	142	0.172	145	0.155
166	0.043	167	0.049	166	0.211	162	0.303
243	0.002	242	0.003	243	0.055	245	0.032
275	0.043	276	0.045	275	0.149	277	0.158
350	0.001	411	0.001	350	0.015	348	0.016
413	0.002	498	0.001	413	0.019	406	0.017
495	0.001	550	0.001	495	0.014	495	0.025
526	0.001	603	0.002	511	0.016	517	0.028
546	0.001	628	0.002	526	0.021	533	0.035
607	0.004	641	0.049	546	0.029	642	0.006
630	0.002	656	0.010	625	0.001	669	0.002

642	0.031	742	0.003	630	0.001	739	0.004
665	0.017	805	0.011	642	0.007	789	0.015
742	0.003	854	0.003	665	0.006	827	0.004
810	0.013	963	0.001	742	0.002	950	0.031
865	0.001	1002	0.004	810	0.008	963	0.062
990	0.001	1076	0.003	990	0.058	1027	0.001
1004	0.001	1134	0.005	1004	0.009	1116	0.002
1009	0.001	1161	0.071	1009	0.015	1171	0.005
1123	0.033	1199	0.008	1043	0.003	1181	0.015
1151	0.004	1200	0.007	1123	0.007	1250	0.001
1185	0.044	1212	0.009	1151	0.010	1315	0.002
1187	0.001	1423	0.040	1185	0.001	1320	0.004
1202	0.003	1439	0.002	1202	0.004	1362	0.008
1208	0.009	1445	0.002	1208	0.018	1397	0.025
1250	0.029	1505	0.053	1312	0.001	1413	0.001
1312	0.003	1520	0.010	1321	0.004	1474	0.006
1323	0.001	1531	0.002	1323	0.003	1499	0.008
1326	0.001	1558	0.132	1326	0.006	1516	0.008
1400	0.076	1583	0.001	1400	0.003	1562	0.002
1411	0.018	1584	0.032	1404	0.016	1590	0.075
1478	0.018	1617	0.007	1411	0.023	1706	0.007
1479	0.004	1751	0.005	1454	0.010	2188	0.004
1481	0.086	1926	0.010	1481	0.001	2471	0.047
1494	0.018	2138	0.039	1494	0.016		
1527	0.009			1527	0.008		
1533	0.009			1533	0.002		
1643	0.005			1629	0.023		
1681	0.003			1643	0.052		
2178	0.003			1681	0.019		
2244	0.026			2178	0.004		
				2244	0.004		

Reference

S1) C. Marian, in *Reviews In Computational Chemistry*, ed. K. Lipkowitz and D. Boyd, Wiley-VCH, Weinheim, **2001**, vol. 17, p. 99.