Supporting Information: An indirect intersystem crossing ($S_1 \rightarrow T_3/T_2 \rightarrow T_1$ promoted by Jahn-Teller effect in cycloparaphenylenes

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Table of contents

Table SI1: Numbering, symmetry and harmonic frequency components of vibrational modes of [6]CPP calculated at B3LYP/6-311G(d) level of theory.

No. (Sym.)	ω(in cm^{-1})	No. (Sym.)	ω(in cm^{-1})	No. (Sym.)	ω(in cm^{-1})	No. (Sym.)	ω(in cm^{-1})
$\nu_1(e_g)$	44.4514	$\nu_{56}(e_g)$	751.4069	$\nu_{111}(a_{1g})$	1274.3500	$\nu_{166}(e_g)$	3180.0595
$\nu_2(e_g)$	44.4514	$\nu_{57}(e_g)$	751.4069	$\nu_{112}(e_g)$	1277.8919	$\nu_{167}(e_u)$	3180.0964
$\nu_3(e_u)$	56.6062	$\nu_{58}(e_u)$	790.1103	$\nu_{113}(e_g)$	1277.8919	$\nu_{168}(e_u)$	3180.0964
$\nu_4(e_u)$	56.6062	$\nu_{59}(e_u)$	790.1103	$\nu_{114}(a_{2u})$	1287.5968	$\nu_{169}(e_g)$	3194.5005
$\nu_5(a_{1g})$	81.7665	$\nu_{60}(a_{1g})$	796.5603	$\nu_{115}(a_{1u})$	1288.9866	$\nu_{170}(e_g)$	3194.5005
$\nu_6(a_{2u})$	93.4553	$\nu_{61}(a_{2u})$	798.8158	$\nu_{116}(e_g)$	1292.4128	$\nu_{171}(a_{2u})$	3194.6168
$\nu_7(a_{1u})$	128.7432	$\nu_{62}(e_g)$	802.5039	$\nu_{117}(e_g)$	1292.4128	$\nu_{172}(e_u)$	3195.2180
$\nu_8(e_g)$	128.7887	$\nu_{63}(e_g)$	802.5039	$\nu_{118}(e_u)$	1298.1926	$\nu_{173}(e_u)$	3195.2180
$\nu_9(e_g)$	128.7887	$\nu_{64}(e_u)$	802.6173	$\nu_{119}(e_u)$	1298.1926	$\nu_{174}(a_{1g})$	3196.0742
$\nu_{10}(e_u)$	149.8526	$\nu_{65}(e_u)$	802.6173	$\nu_{120}(a_{1g})$	1307.9507		
$\nu_{11}(e_u)$	149.8526	$\nu_{66}(a_{1g})$	810.4361	$\nu_{121}(a_{2g})$	1323.4560		
$\nu_{12}(a_{2u})$	173.0082	$\nu_{67}(a_{1g})$	824.9542	$\nu_{122}(e_u)$	1339.4788		
$\nu_{13}(a_{2g})$	183.0516	$\nu_{68}(e_u)$	835.3565	$\nu_{123}(e_u)$	1339.4788		
$\nu_{14}(a_{1g})$	217.8053	$\nu_{69}(e_u)$	835.3565	$\nu_{124}(a_{1u})$	1344.3829		
$\nu_{15}(e_g)$	243.7451	$\nu_{70}(e_g)$	859.0929	$\nu_{125}(e_g)$	1348.1640		
$\nu_{16}(e_g)$	243.7451	$\nu_{71}(e_g)$	859.0929	$\nu_{126}(e_g)$	1348.1640		
$\nu_{17}(e_u)$	290.4859	$\nu_{72}(a_{2u})$	868.2810	$\nu_{127}(e_g)$	1420.3101		
$\nu_{18}(e_u)$	290.4859	$\nu_{73}(a_{2g})$	950.0721	$\nu_{128}(e_g)$	1420.3101		
$\nu_{19}(a_{1g})$	316.9239	$\nu_{74}(e_g)$	950.1736	$\nu_{129}(a_{2u})$	1420.9239		
$\nu_{20}(e_u)$	331.4909	$\nu_{75}(e_g)$	950.1736	$\nu_{130}(e_u)$	1437.4522		
$\nu_{21}(e_u)$	331.4909	$\nu_{76}(a_{1u})$	950.3627	$\nu_{131}(e_u)$	1437.4522		
$\nu_{22}(e_g)$	383.1084	$\nu_{77}(e_u)$	950.5615	$\nu_{132}(a_{1g})$	1457.3563		
$\nu_{23}(e_g)$	383.1084	$\nu_{78}(e_u)$	950.5615	$\nu_{133}(a_{2g})$	1513.8538		
$\nu_{24}(e_u)$	386.8259	$\nu_{79}(a_{1u})$	959.3742	$\nu_{134}(e_u)$	1524.3766		
$\nu_{25}(e_u)$	383.8259	$\nu_{80}(e_g)$	959.5074	$\nu_{135}(e_u)$	1524.3766		
$\nu_{26}(a_{1u})$	391.9137	$\nu_{81}(e_g)$	959.5074	$\nu_{136}(e_g)$	1541.3762		
$\nu_{27}(a_{2g})$	395.4625	$\nu_{82}(a_{2g})$	960.2294	$\nu_{137}(e_g)$	1541.3762		
$\nu_{28}(e_u)$	436.5558	$\nu_{83}(e_u)$	960.2313	$\nu_{138}(a_{2g})$	1548.5169		
$\nu_{29}(e_u)$	436.5558	$\nu_{84}(e_u)$	960.2313	$\nu_{139}(a_{1u})$	1549.2197		
$\nu_{30}(a_{2g})$	446.7702	$\nu_{85}(a_{2g})$	1012.2287	$\nu_{140}(e_u)$	1565.9451		
$\nu_{31}(e_g)$	449.7504	$\nu_{86}(e_u)$	1015.8353	$\nu_{141}(e_u)$	1565.9451		
$\nu_{32}(e_g)$	449.7504	$\nu_{87}(e_u)$	1015.8353	$\nu_{142}(e_g)$	1588.4171		
$\nu_{33}(e_g)$	481.2724	$\nu_{88}(a_{2u})$	1018.8256	$\nu_{143}(e_g)$	1588.4171		
$\nu_{34}(e_g)$	481.2724	$\nu_{89}(e_g)$	1020.7540	$\nu_{144}(a_{1u})$	1596.7508		
$\nu_{35}(a_{1u})$	502.9848	$\nu_{90}(e_g)$	1020.7540	$\nu_{145}(a_{1g})$	1615.1353		
$\nu_{36}(a_{1g})$	521.9691	$\nu_{91}(a_{1u})$	1031.4825	$\nu_{146}(e_u)$	1619.6380		
$\nu_{37}(e_u)$	558.4089	$\nu_{92}(e_g)$	1040.5467	$\nu_{147}(e_u)$	1619.6380		
$\nu_{38}(e_u)$	558.4089	$\nu_{93}(e_g)$	1040.5467	$\nu_{148}(e_g)$	1634.9738		
$\nu_{39}(a_{1u})$	563.2768	$\nu_{94}(e_u)$	1060.4027	$\nu_{149}(e_g)$	1634.9738		
$\nu_{40}(a_{2u})$	566.9748	$\nu_{95}(e_u)$	1060.4027	$\nu_{150}(a_{2u})$	1640.7495		
$\nu_{41}(e_g)$	588.6013	$\nu_{96}(a_{2g})$	1067.7114	$\nu_{151}(a_{2g})$	3157.7107		
$\nu_{42}(e_g)$	588.6013	$\nu_{97}(a_{2u})$	1142.4151	$\nu_{152}(a_{1u})$	3157.8452		
$\nu_{43}(a_{1u})$	633.8416	$\nu_{98}(e_g)$	1142.9883	$\nu_{153}(e_g)$	3158.3580		
$\nu_{44}(e_g)$	641.3636	$\nu_{99}(e_g)$	1142.9883	$\nu_{154}(e_g)$	3158.3580		
$\nu_{45}(e_g)$	641.3636	$\nu_{100}(a_{1g})$	1143.4060	$\nu_{155}(e_u)$	3158.4217		
$\nu_{46}(a_{2u})$	649.3901	$\nu_{101}(e_u)$	1143.5450	$\nu_{156}(e_u)$	3158.4217		
$\nu_{47}(e_u)$	652.2575	$\nu_{102}(e_u)$	1143.5450	$\nu_{157}(e_g)$	3173.1203		
$\nu_{48}(e_u)$	652.2575	$\nu_{103}(a_{2u})$	1214.3533	$\nu_{158}(e_g)$	3173.1203		
$\nu_{49}(a_{2g})$	657.2116	$\nu_{104}(e_g)$	1218.3481	$\nu_{159}(e_u)$	3173.2085		
$\nu_{50}(e_g)$	692.4795	$\nu_{105}(e_g)$	1218.3481	$\nu_{160}(e_u)$	3173.2085		
$\nu_{51}(e_g)$	692.4795	$\nu_{106}(a_{1g})$	1221.0331	$\nu_{161}(a_{1g})$	3175.9705		
$\nu_{52}(e_u)$	730.2262	$\nu_{107}(e_u)$	1222.5793	$\nu_{162}(a_{2u})$	3176.4407		
$\nu_{53}(e_u)$	730.2262	$\nu_{108}(e_u)$	1222.5793	$\nu_{163}(a_{1u})$	3176.8895		
$\nu_{54}(a_{2g})$	741.3468	$\nu_{109}(e_u)$	1269.8687	$\nu_{164}(a_{2g})$	3177.6232		
$\nu_{55}(a_{1u})$	743.3292	$\nu_{110}(e_u)$	1269.8687	$\nu_{165}(e_g)$	3180.0595		

Table SI2: Numbering, symmetry and harmonic frequency components of vibrational modes of [8]CPP calculated at B3LYP/6-311G(d) level of theory.

No. (Sym.)	ω(in cm^{-1})	No. (Sym.)	ω(in cm^{-1})	No. (Sym.)	ω(in cm^{-1})	No. (Sym.)	ω(in cm^{-1})
$\nu_{1}(e_2)$	25.1303	$\nu_{61}(e_3)$	642.0701	$\nu_{121}(e_3)$	1021.7900	$\nu_{181}(e_1)$	1526.8979
$\nu_{2}(e_2)$	25.1303	$\nu_{62}(b_2)$	643.0291	$\nu_{122}(e_3)$	1021.7900	$\nu_{182}(e_2)$	1540.7996
$\nu_{3}(e_2)$	37.3102	$\nu_{63}(e_2)$	650.7106	$\nu_{123}(b_1)$	1034.6303	$\nu_{183}(e_2)$	1540.7996
$\nu_{4}(e_2)$	37.3102	$\nu_{64}(e_2)$	650.7106	$\nu_{124}(e_3)$	1038.5122	$\nu_{184}(e_3)$	1553.4602
$\nu_{5}(e_3)$	63.9065	$\nu_{65}(e_1)$	657.6105	$\nu_{125}(e_3)$	1038.5122	$\nu_{185}(e_3)$	1553.4602
$\nu_{6}(e_3)$	63.9065	$\nu_{66}(e_1)$	657.6105	$\nu_{126}(e_2)$	1053.2684	$\nu_{186}(a_2)$	1555.8039
$\nu_{7}(e_1)$	74.5509	$\nu_{67}(a_2)$	660.2017	$\nu_{127}(e_2)$	1053.2684	$\nu_{187}(b_1)$	1558.4682
$\nu_{8}(e_1)$	74.5509	$\nu_{68}(e_3)$	683.1501	$\nu_{128}(e_1)$	1067.0965	$\nu_{188}(e_1)$	1566.8019
$\nu_{9}(b_2)$	75.9043	$\nu_{69}(e_3)$	683.1501	$\nu_{129}(e_1)$	1067.0965	$\nu_{189}(e_1)$	1566.8019
$\nu_{10}(a_1)$	86.2280	$\nu_{70}(e_2)$	726.1924	$\nu_{130}(a_2)$	1071.8839	$\nu_{190}(e_2)$	1585.8405
$\nu_{11}(e_3)$	102.5486	$\nu_{71}(e_2)$	726.1924	$\nu_{131}(b_2)$	1142.4320	$\nu_{191}(e_2)$	1585.8405
$\nu_{12}(e_3)$	102.5486	$\nu_{72}(b_1)$	742.7050	$\nu_{132}(a_3)$	1143.3365	$\nu_{192}(e_3)$	1599.7654
$\nu_{13}(e_2)$	114.4535	$\nu_{73}(e_3)$	746.4134	$\nu_{133}(e_3)$	1143.3365	$\nu_{193}(e_3)$	1599.7654
$\nu_{14}(e_2)$	114.4535	$\nu_{74}(e_3)$	746.4134	$\nu_{134}(e_2)$	1145.1334	$\nu_{194}(b_1)$	1604.6488
$\nu_{15}(b_1)$	136.0854	$\nu_{75}(e_1)$	749.1926	$\nu_{135}(e_2)$	1145.1334	$\nu_{195}(a_1)$	1626.9281
$\nu_{16}(e_1)$	151.0386	$\nu_{76}(e_1)$	749.1926	$\nu_{136}(e_1)$	1146.1820	$\nu_{196}(e_1)$	1630.4475
$\nu_{17}(e_1)$	151.0386	$\nu_{77}(a_2)$	758.4505	$\nu_{137}(e_1)$	1146.1820	$\nu_{197}(e_1)$	1630.4475
$\nu_{18}(b_2)$	162.3342	$\nu_{78}(e_2)$	769.4862	$\nu_{138}(a_1)$	1146.4152	$\nu_{198}(e_2)$	1640.0320
$\nu_{19}(a_1)$	166.2229	$\nu_{79}(e_2)$	769.4862	$\nu_{139}(b_2)$	1216.2466	$\nu_{199}(e_2)$	1640.0320
$\nu_{20}(a_2)$	185.0506	$\nu_{80}(e_1)$	802.7620	$\nu_{140}(e_3)$	1218.2115	$\nu_{200}(e_3)$	1647.3870
$\nu_{21}(e_3)$	224.1542	$\nu_{81}(e_1)$	802.7620	$\nu_{141}(e_3)$	1218.2115	$\nu_{201}(e_3)$	1647.3870
$\nu_{22}(e_3)$	224.1542	$\nu_{82}(a_1)$	807.9420	$\nu_{142}(e_2)$	1222.5838	$\nu_{202}(b_2)$	1649.9101
$\nu_{23}(e_1)$	226.9720	$\nu_{83}(e_1)$	818.3737	$\nu_{143}(e_2)$	1222.5838	$\nu_{203}(a_2)$	3160.5090
$\nu_{24}(e_1)$	226.9720	$\nu_{84}(e_1)$	818.3737	$\nu_{144}(a_1)$	1223.6138	$\nu_{204}(b_1)$	3160.6574
$\nu_{25}(e_2)$	298.5393	$\nu_{85}(b_2)$	818.9581	$\nu_{145}(e_1)$	1224.1989	$\nu_{205}(e_3)$	3161.1027
$\nu_{26}(e_2)$	298.5393	$\nu_{86}(e_3)$	820.0416	$\nu_{146}(e_1)$	1224.1989	$\nu_{206}(e_3)$	3161.1027
$\nu_{27}(a_1)$	307.0197	$\nu_{87}(e_3)$	820.0416	$\nu_{147}(e_2)$	1283.9565	$\nu_{207}(e_1)$	3161.1655
$\nu_{28}(e_1)$	335.4972	$\nu_{88}(e_2)$	820.7783	$\nu_{148}(e_2)$	1283.9565	$\nu_{208}(e_1)$	3161.1655
$\nu_{29}(e_1)$	335.4972	$\nu_{89}(e_2)$	820.7783	$\nu_{149}(b_2)$	1284.1368	$\nu_{209}(e_2)$	3161.6311
$\nu_{30}(e_2)$	344.5141	$\nu_{90}(a_1)$	821.9496	$\nu_{150}(e_3)$	1284.2444	$\nu_{210}(e_2)$	3161.6311
$\nu_{31}(e_2)$	344.5141	$\nu_{91}(a_1)$	825.0777	$\nu_{151}(e_3)$	1284.2444	$\nu_{211}(e_2)$	3171.6722
$\nu_{32}(e_1)$	395.3843	$\nu_{92}(e_1)$	832.5764	$\nu_{152}(e_1)$	1285.0508	$\nu_{212}(e_2)$	3171.6722
$\nu_{33}(e_1)$	395.3843	$\nu_{93}(e_1)$	832.5764	$\nu_{153}(e_1)$	1285.0508	$\nu_{213}(e_3)$	3172.7229
$\nu_{34}(e_3)$	401.9230	$\nu_{94}(e_2)$	852.7451	$\nu_{154}(a_1)$	1287.6794	$\nu_{214}(e_3)$	3172.7229
$\nu_{35}(e_3)$	401.9230	$\nu_{95}(e_2)$	852.7451	$\nu_{155}(e_2)$	1299.0948	$\nu_{215}(e_1)$	3173.1603
$\nu_{36}(a_2)$	402.8744	$\nu_{96}(e_3)$	868.2964	$\nu_{156}(e_2)$	1299.0948	$\nu_{216}(e_1)$	3173.1603
$\nu_{37}(e_2)$	403.3478	$\nu_{97}(e_3)$	868.2964	$\nu_{157}(e_3)$	1299.5444	$\nu_{217}(b_1)$	3174.2010
$\nu_{38}(e_2)$	403.3478	$\nu_{98}(b_2)$	873.7429	$\nu_{158}(e_3)$	1299.5444	$\nu_{218}(a_2)$	3175.0294
$\nu_{39}(b_1)$	406.7471	$\nu_{99}(b_1)$	954.1883	$\nu_{159}(b_1)$	1301.3017	$\nu_{219}(a_1)$	3178.3332
$\nu_{40}(e_1)$	425.1316	$\nu_{100}(e_3)$	954.7030	$\nu_{160}(e_1)$	1306.3929	$\nu_{220}(b_2)$	3179.1774
$\nu_{41}(e_1)$	425.1316	$\nu_{101}(e_3)$	954.7030	$\nu_{161}(e_1)$	1306.3929	$\nu_{221}(e_1)$	3180.0449
$\nu_{42}(a_2)$	445.8214	$\nu_{102}(e_2)$	955.9835	$\nu_{162}(a_1)$	1315.6732	$\nu_{222}(e_1)$	3180.0449
$\nu_{43}(e_2)$	447.3231	$\nu_{103}(e_2)$	955.9835	$\nu_{163}(a_2)$	1326.6665	$\nu_{223}(e_3)$	3180.5323
$\nu_{44}(e_2)$	447.3231	$\nu_{104}(e_1)$	956.8874	$\nu_{164}(e_1)$	1338.3215	$\nu_{224}(e_3)$	3180.5323
$\nu_{45}(e_3)$	468.3435	$\nu_{105}(e_1)$	956.8874	$\nu_{165}(e_1)$	1338.3215	$\nu_{225}(e_2)$	3181.3986
$\nu_{46}(e_3)$	468.3435	$\nu_{106}(a_2)$	957.0445	$\nu_{166}(b_1)$	1347.5331	$\nu_{226}(e_2)$	3181.3986
$\nu_{47}(e_3)$	491.1150	$\nu_{107}(e_3)$	962.4486	$\nu_{167}(e_2)$	1349.2392	$\nu_{227}(e_3)$	3191.4508
$\nu_{48}(e_3)$	491.1150	$\nu_{108}(e_3)$	962.4486	$\nu_{168}(e_2)$	1349.2392	$\nu_{228}(e_3)$	3191.4508
$\nu_{49}(b_1)$	501.4698	$\nu_{109}(b_1)$	962.7078	$\nu_{169}(e_3)$	1349.7359	$\nu_{229}(b_2)$	3191.6316
$\nu_{50}(a_1)$	512.9050	$\nu_{110}(e_2)$	962.8818	$\nu_{170}(e_3)$	1349.7359	$\nu_{230}(e_2)$	3191.7235
$\nu_{51}(e_1)$	540.7716	$\nu_{111}(e_2)$	962.8818	$\nu_{171}(e_3)$	1425.4557	$\nu_{231}(e_2)$	3191.7235
$\nu_{52}(e_1)$	540.7716	$\nu_{112}(e_1)$	963.6542	$\nu_{172}(e_3)$	1425.4557	$\nu_{232}(e_1)$	3192.7430
$\nu_{53}(b_1)$	554.9607	$\nu_{113}(e_1)$	963.6542	$\nu_{173}(b_2)$	1425.6951	$\nu_{233}(e_1)$	3192.7430
$\nu_{54}(e_2)$	573.2120	$\nu_{114}(a_2)$	963.7141	$\nu_{174}(e_2)$	1431.8502	$\nu_{234}(a_1)$	3193.4331
$\nu_{55}(e_2)$	573.2120	$\nu_{115}(a_2)$	1015.4975	$\nu_{175}(e_2)$	1431.8502		
$\nu_{56}(b_2)$	577.2543	$\nu_{116}(e_1)$	1017.7835	$\nu_{176}(e_1)$	1449.9730		
$\nu_{57}(e_3)$	589.2322	$\nu_{117}(e_1)$	1017.7835	$\nu_{177}(e_1)$	1449.9730		
$\nu_{58}(e_3)$	589.2322	$\nu_{118}(b_2)$	1018.4755	$\nu_{178}(a_1)$	1462.1358		
$\nu_{59}(b_1)$	637.1182	$\nu_{119}(e_2)$	1021.3942	$\nu_{179}(a_2)$	1519.7245		
$\nu_{60}(e_3)$	642.0701	$\nu_{120}(e_2)$	1021.3942	$\nu_{180}(e_1)$	1526.8979		

Table SI3: Numbering, symmetry and harmonic frequency components of vibrational modes of [10]CPP calculated at B3LYP/6-311G(d) level of theory.

No. (Sym.)	ω(in cm^{-1})	No. (Sym.)	ω(in cm^{-1})	No. (Sym.)	ω(in cm^{-1})	No. (Sym.)	ω(in cm^{-1})	No. (Sym.)	ω(in cm^{-1})
$\nu_{1}(e_{2g})$	16.3527	$\nu_{61}(e_{1g})$	499.8187	$\nu_{121}(e_{2u})$	862.1187	$\nu_{181}(e_{2g})$	1222.0078	$\nu_{241}(e_{2u})$	1595.8140
$\nu_{2}(e_{2g})$	16.3527	$\nu_{62}(e_{1g})$	499.8187	$\nu_{122}(e_{1g})$	872.6538	$\nu_{182}(a_{1g})$	1222.5293	$\nu_{242}(e_{1g})$	1604.9999
$\nu_{3}(e_{2u})$	25.5479	$\nu_{63}(a_{1u})$	502.0556	$\nu_{123}(e_{1g})$	872.6538	$\nu_{183}(e_{1u})$	1222.6588	$\nu_{243}(e_{1g})$	1604.9999
$\nu_{4}(e_{2u})$	25.5479	$\nu_{64}(a_{1g})$	510.0529	$\nu_{124}(a_{2u})$	876.2147	$\nu_{184}(e_{1u})$	1222.6588	$\nu_{244}(a_{1u})$	1608.1610
$\nu_{5}(e_{2u})$	45.0056	$\nu_{65}(e_{1u})$	531.2672	$\nu_{125}(a_{1u})$	956.6335	$\nu_{185}(a_{2u})$	1282.3331	$\nu_{245}(a_{1g})$	1633.7876
$\nu_{6}(e_{2u})$	45.0056	$\nu_{66}(e_{1u})$	531.2672	$\nu_{126}(e_{1g})$	957.3896	$\nu_{186}(e_{1g})$	1283.2502	$\nu_{246}(e_{1u})$	1635.9156
$\nu_{7}(a_{2u})$	59.5593	$\nu_{67}(a_{1u})$	550.2661	$\nu_{127}(e_{1g})$	957.3896	$\nu_{187}(e_{1g})$	1283.2502	$\nu_{247}(e_{1u})$	1635.9156
$\nu_{8}(e_{2g})$	60.5053	$\nu_{68}(e_{2g})$	560.2300	$\nu_{128}(a_{2g})$	958.0612	$\nu_{188}(e_{2u})$	1285.9022	$\nu_{248}(e_{2g})$	1642.0155
$\nu_{9}(e_{2g})$	60.5053	$\nu_{69}(e_{2g})$	560.2300	$\nu_{129}(e_{1u})$	958.4543	$\nu_{189}(e_{2u})$	1285.9022	$\nu_{249}(e_{2g})$	1642.0155
$\nu_{10}(e_{1g})$	61.6761	$\nu_{70}(e_{2u})$	580.6062	$\nu_{130}(e_{1u})$	958.4543	$\nu_{190}(e_{2g})$	1289.0538	$\nu_{250}(e_{2u})$	1648.3581
$\nu_{11}(e_{1g})$	61.6761	$\nu_{71}(e_{2u})$	580.6062	$\nu_{131}(e_{2u})$	958.9807	$\nu_{191}(e_{2g})$	1289.0538	$\nu_{251}(e_{2u})$	1648.3581
$\nu_{12}(e_{1u})$	83.8873	$\nu_{72}(a_{2u})$	582.6214	$\nu_{132}(e_{2u})$	958.9807	$\nu_{192}(e_{1u})$	1292.1372	$\nu_{252}(e_{1g})$	1652.4769
$\nu_{13}(e_{1u})$	83.8873	$\nu_{73}(e_{1g})$	590.1243	$\nu_{133}(e_{2g})$	959.1369	$\nu_{193}(e_{1u})$	1292.1372	$\nu_{253}(e_{1g})$	1652.4769
$\nu_{14}(a_{1g})$	88.8637	$\nu_{74}(e_{1g})$	590.1243	$\nu_{134}(e_{2g})$	959.1369	$\nu_{194}(a_{1g})$	1294.0164	$\nu_{254}(a_{2u})$	1653.8519
$\nu_{15}(e_{2u})$	93.4581	$\nu_{75}(a_{1u})$	638.9520	$\nu_{135}(e_{2u})$	962.4521	$\nu_{195}(e_{2u})$	1301.8086	$\nu_{255}(a_{2g})$	3161.3647
$\nu_{16}(e_{2u})$	93.4581	$\nu_{76}(a_{2u})$	639.4875	$\nu_{136}(e_{2u})$	962.4521	$\nu_{196}(e_{2u})$	1301.8086	$\nu_{256}(a_{1u})$	3161.4921
$\nu_{17}(e_{1g})$	101.3390	$\nu_{77}(e_{1g})$	642.4885	$\nu_{137}(e_{1g})$	962.8462	$\nu_{197}(e_{2g})$	1303.3146	$\nu_{257}(e_{1g})$	3161.8054
$\nu_{18}(e_{1g})$	101.3390	$\nu_{78}(e_{1g})$	642.4885	$\nu_{138}(e_{1g})$	962.8462	$\nu_{198}(e_{2g})$	1303.3146	$\nu_{258}(e_{1g})$	3161.8054
$\nu_{19}(e_{2g})$	118.6380	$\nu_{79}(e_{2u})$	649.3988	$\nu_{139}(a_{1u})$	963.4164	$\nu_{199}(e_{1g})$	1304.0326	$\nu_{259}(e_{1u})$	3161.8678
$\nu_{20}(e_{2g})$	118.6380	$\nu_{80}(e_{2u})$	649.3988	$\nu_{140}(e_{2g})$	964.1687	$\nu_{200}(e_{1g})$	1304.0326	$\nu_{260}(e_{1u})$	3161.8678
$\nu_{21}(a_{1g})$	135.1052	$\nu_{81}(e_{2g})$	655.6806	$\nu_{141}(e_{2g})$	964.1687	$\nu_{201}(a_{1u})$	1305.3135	$\nu_{261}(e_{2u})$	3162.3892
$\nu_{22}(a_{1u})$	141.7596	$\nu_{82}(a_{2g})$	655.6806	$\nu_{142}(e_{1u})$	966.0315	$\nu_{202}(e_{1u})$	1310.7709	$\nu_{262}(e_{2u})$	3162.3892
$\nu_{23}(e_{1u})$	157.4940	$\nu_{83}(e_{1u})$	660.0144	$\nu_{143}(e_{1u})$	966.0315	$\nu_{203}(e_{1u})$	1310.7709	$\nu_{263}(e_{2g})$	3162.4387
$\nu_{24}(e_{1u})$	157.4940	$\nu_{84}(e_{1u})$	660.0144	$\nu_{144}(a_{2g})$	966.6382	$\nu_{204}(a_{1g})$	1318.7886	$\nu_{264}(e_{2g})$	3162.4387
$\nu_{25}(a_{2u})$	160.7181	$\nu_{85}(a_{2g})$	661.5310	$\nu_{145}(a_{2g})$	1017.3332	$\nu_{205}(a_{2g})$	1326.8506	$\nu_{265}(e_{2u})$	3171.2178
$\nu_{26}(e_{1u})$	185.2421	$\nu_{86}(e_{1g})$	673.0265	$\nu_{146}(a_{2u})$	1018.4088	$\nu_{206}(e_{1u})$	1335.9494	$\nu_{266}(e_{2u})$	3171.2178
$\nu_{27}(e_{1u})$	185.2421	$\nu_{87}(e_{1g})$	673.0265	$\nu_{147}(e_{1u})$	1018.9252	$\nu_{207}(e_{1u})$	1335.9494	$\nu_{267}(e_{2g})$	3171.4255
$\nu_{28}(a_{2g})$	186.6798	$\nu_{88}(e_{2u})$	718.2947	$\nu_{148}(e_{1u})$	1018.9252	$\nu_{208}(e_{2g})$	1345.8531	$\nu_{268}(e_{2g})$	3171.4255
$\nu_{29}(e_{1g})$	211.8639	$\nu_{89}(e_{2u})$	718.2947	$\nu_{149}(e_{1g})$	1021.1687	$\nu_{209}(e_{2g})$	1345.8531	$\nu_{269}(e_{1g})$	3172.3335
$\nu_{30}(e_{1g})$	211.8639	$\nu_{90}(e_{2g})$	742.8745	$\nu_{150}(e_{1g})$	1021.1687	$\nu_{210}(a_{1u})$	1347.4971	$\nu_{270}(e_{1g})$	3172.3335
$\nu_{31}(e_{2u})$	274.2458	$\nu_{91}(e_{2g})$	742.8745	$\nu_{151}(e_{2g})$	1021.5889	$\nu_{211}(e_{1g})$	1348.8602	$\nu_{271}(e_{1u})$	3172.9306
$\nu_{32}(e_{2u})$	274.2458	$\nu_{92}(a_{1u})$	742.9392	$\nu_{152}(e_{2g})$	1021.5889	$\nu_{212}(e_{1g})$	1348.8602	$\nu_{272}(e_{1u})$	3172.9306
$\nu_{33}(e_{2g})$	280.3606	$\nu_{93}(e_{1g})$	744.7655	$\nu_{153}(e_{2u})$	1023.2453	$\nu_{213}(e_{2u})$	1350.0738	$\nu_{273}(a_{1u})$	3173.1557
$\nu_{34}(e_{2g})$	280.3606	$\nu_{94}(e_{1g})$	744.7655	$\nu_{154}(e_{2u})$	1023.2453	$\nu_{214}(e_{2u})$	1350.0738	$\nu_{274}(a_{2g})$	3173.9879
$\nu_{35}(a_{1g})$	302.1504	$\nu_{95}(e_{2u})$	755.7787	$\nu_{155}(a_{1u})$	1036.2979	$\nu_{215}(a_{2u})$	1426.9058	$\nu_{275}(a_{1g})$	3178.9516
$\nu_{36}(e_{1u})$	327.8011	$\nu_{96}(e_{2u})$	755.7787	$\nu_{156}(e_{1g})$	1038.3700	$\nu_{216}(e_{1g})$	1426.9233	$\nu_{276}(e_{1u})$	3179.9124
$\nu_{37}(e_{1u})$	327.8011	$\nu_{97}(e_{1u})$	759.0625	$\nu_{157}(e_{1g})$	1038.3700	$\nu_{217}(e_{1g})$	1426.9233	$\nu_{277}(e_{1u})$	3179.9124
$\nu_{38}(e_{2g})$	332.6758	$\nu_{98}(e_{1u})$	759.0625	$\nu_{158}(e_{2u})$	1047.5750	$\nu_{218}(e_{2u})$	1429.9047	$\nu_{278}(a_{2u})$	3179.9311
$\nu_{39}(e_{2g})$	332.6758	$\nu_{99}(a_{2g})$	766.2195	$\nu_{159}(e_{2u})$	1047.5750	$\nu_{219}(e_{2u})$	1429.9047	$\nu_{279}(e_{1g})$	3180.6693
$\nu_{40}(e_{2u})$	382.0000	$\nu_{100}(e_{2g})$	783.3283	$\nu_{160}(e_{2g})$	1060.6584	$\nu_{220}(e_{1u})$	1440.3794	$\nu_{280}(e_{1g})$	3180.6693
$\nu_{41}(e_{2u})$	382.0000	$\nu_{101}(e_{2g})$	783.3283	$\nu_{161}(e_{2g})$	1060.6584	$\nu_{221}(e_{2g})$	1440.3794	$\nu_{281}(e_{2g})$	3181.2817
$\nu_{42}(e_{2g})$	398.7141	$\nu_{102}(e_{1u})$	807.0146	$\nu_{162}(e_{1u})$	1070.2525	$\nu_{222}(e_{2g})$	1455.4340	$\nu_{282}(e_{2g})$	3181.2817
$\nu_{43}(e_{2g})$	398.7141	$\nu_{103}(e_{1u})$	807.0146	$\nu_{163}(e_{1u})$	1070.2525	$\nu_{223}(e_{1u})$	1455.4340	$\nu_{283}(e_{2u})$	3181.5861
$\nu_{44}(e_{1u})$	404.5523	$\nu_{104}(a_{1g})$	810.7507	$\nu_{164}(a_{2g})$	1073.5035	$\nu_{224}(a_{1g})$	1463.3778	$\nu_{284}(e_{2u})$	3181.5861
$\nu_{45}(e_{1u})$	404.5523	$\nu_{105}(a_{1g})$	823.7978	$\nu_{165}(a_{2u})$	1141.2110	$\nu_{225}(a_{2g})$	1522.1891	$\nu_{285}(e_{1g})$	3190.1861
$\nu_{46}(a_{2g})$	406.9930	$\nu_{106}(e_{1u})$	826.5183	$\nu_{166}(e_{1g})$	1141.9657	$\nu_{226}(e_{1u})$	1527.2339	$\nu_{286}(e_{1g})$	3190.1861
$\nu_{47}(e_{1g})$	412.0499	$\nu_{107}(e_{1u})$	826.5183	$\nu_{167}(e_{1g})$	1141.9657	$\nu_{227}(e_{1u})$	1527.2339	$\nu_{287}(e_{2u})$	3190.2239
$\nu_{48}(e_{1g})$	412.0499	$\nu_{108}(a_{2u})$	827.7221	$\nu_{168}(e_{2u})$	1143.7530	$\nu_{228}(e_{2g})$	1537.8664	$\nu_{288}(e_{2u})$	3190.2239
$\nu_{49}(a_{1u})$	414.7000	$\nu_{109}(e_{1g})$	828.2611	$\nu_{169}(e_{2u})$	1143.7530	$\nu_{229}(e_{2g})$	1537.8664	$\nu_{289}(a_{2u})$	3190.3282
$\nu_{50}(e_{2u})$	416.5514	$\nu_{110}(e_{1g})$	828.2611	$\nu_{170}(e_{2g})$	1145.4330	$\nu_{230}(e_{2u})$	1549.7774	$\nu_{290}(e_{2g})$	3190.8600
$\nu_{51}(e_{2u})$	416.5514	$\nu_{111}(e_{2g})$	829.0918	$\nu_{171}(e_{2g})$	1145.4330	$\nu_{231}(e_{2u})$	1549.7774	$\nu_{291}(e_{2g})$	3190.8600
$\nu_{52}(e_{1u})$	425.4135	$\nu_{112}(e_{2g})$	829.0918	$\nu_{172}(e_{1u})$	1146.3581	$\nu_{232}(e_{1g})$	1558.8971	$\nu_{292}(e_{1u})$	3191.7796
$\nu_{53}(e_{1u})$	425.4135	$\nu_{113}(e_{2u})$	829.1816	$\nu_{173}(e_{1u})$	1146.3581	$\nu_{233}(e_{1g})$	1558.8971	$\nu_{293}(e_{1u})$	3191.7796
$\nu_{54}(e_{2g})$	429.2076	$\nu_{114}(e_{2u})$	829.1816	$\nu_{174}(a_{1g})$	1146.6256	$\nu_{234}(a_{2g})$	1559.7947	$\nu_{294}(a_{1g})$	3192.2669
$\nu_{55}(e_{2g})$	429.2076	$\nu_{115}(a_{1g})$	830.9109	$\nu_{175}(a_{2u})$	1215.4162	$\nu_{235}(a_{1u})$	1562.2907		
$\nu_{56}(a_{2g})$	446.9057	$\nu_{116}(e_{1u})$	831.4573	$\nu_{176}(e_{1g})$	1216.5158	$\nu_{236}(e_{1u})$	1567.0621		
$\nu_{57}(e_{2u})$	462.4208	$\nu_{117}(e_{1u})$	831.4573	$\nu_{177}(e_{1g})$	1216.5158	$\nu_{237}(e_{1u})$	1567.0621		
$\nu_{58}(e_{2u})$	462.4208	$\nu_{118}(e_{2g})$	846.0223	$\nu_{178}(e_{2u})$	1219.3449	$\nu_{238}(e_{2g})$	1581.9154		
$\nu_{59}(e_{1g})$	480.8670	$\nu_{119}(e_{2g})$	846.0223	$\nu_{179}(e_{2u})$	1219.3449	$\nu_{239}(e_{2g})$	1581.9154		
$\nu_{60}(e_{1g})$	480.8670	$\nu_{120}(e_{2u})$	862.1187	$\nu_{180}(e_{2g})$	1222.0078	$\nu_{240}(e_{2u})$	1595.8140		

Table SI4: Linear intrastate coupling parameters (κ) of T_1 and T_2 states of CPP derived at TD-B3LYP/6-311G(d) level of theory. All values are in eV. The coupling strength ($\kappa^2/2\omega^2$) is given in the paranthesis.

[6]CPP			[8]CPP			[10]CPP		
a_{1g} mode	κ^{T_1}	κ^{T_2}	a_1 mode	κ^{T_1}	κ^{T_2}	a_{1g} mode	κ^{T_1}	κ^{T_2}
ν_5 [0.0101]	-0.0745 (27.20)	-0.0394 (7.61)	ν_{10} [0.0107]	-0.0684 (20.43)	-0.0492 (10.57)	ν_{14} [0.0110]	-0.0595 (14.63)	-0.0498 (10.25)
ν_{14} [0.0270]	-0.0301 (0.62)	-0.0146 (0.15)	ν_{19} [0.0206]	0.0265 (0.83)	0.0183 (0.39)	ν_{21} [0.0168]	0.0276 (1.35)	0.0226 (0.90)
ν_{19} [0.0393]	0.0400 (0.52)	0.0248 (0.20)	ν_{27} [0.0381]	0.0272 (0.25)	0.0210 (0.15)	ν_{35} [0.0375]	0.0196 (0.14)	0.0170 (0.10)
ν_{36} [0.0647]	0.0500 (0.30)	0.0337 (0.14)	ν_{50} [0.0636]	-0.0266 (0.09)	-0.0216 (0.06)	ν_{64} [0.0632]	0.0168 (0.04)	0.0150 (0.03)
ν_{60} [0.0998]	-0.0264 (0.03)	-0.0113 (0.01)	ν_{82} [0.1002]	0.0226 (0.03)	0.0210 (0.02)	ν_{104}[0.1005]	0.0219 (0.02)	0.0220 (0.02)
ν_{66} [0.1005]	0.0052 (0.00)	-0.0114 (0.01)	ν_{90} [0.1019]	-0.0079 (0.00)	-0.0174 (0.01)	ν_{105}[0.1021]	0.0364 (0.06)	0.0372 (0.07)
ν_{67} [0.1023]	-0.0634 (0.19)	-0.0644 (0.20)	ν_{91} [0.1023]	-0.0412 (0.08)	-0.0377 (0.07)	ν_{115}[0.1030]	0.0208 (0.02)	0.0157 (0.01)
ν_{100}[0.1418]	-0.0205 (0.01)	-0.0140 (0.01)	ν_{138}[0.1423]	0.0127 (0.00)	0.0104 (0.00)	ν_{174}[0.1422]	0.0084 (0.00)	0.0076 (0.00)
ν_{106}[0.1514]	-0.1360 (0.40)	-0.0992 (0.21)	ν_{144}[0.1517]	-0.1002 (0.22)	-0.0852 (0.16)	ν_{182}[0.1516]	-0.0812 (0.14)	-0.0744 (0.12)
ν_{111}[0.1580]	-0.0848 (0.14)	-0.0578 (0.07)	ν_{154}[0.1597]	0.0759 (0.11)	0.0630 (0.08)	ν_{194}[0.1604]	-0.0667 (0.09)	-0.0605 (0.07)
ν_{120}[0.1622]	-0.0329 (0.02)	-0.0199 (0.01)	ν_{162}[0.1613]	-0.0293 (0.02)	-0.0231 (0.01)	ν_{204}[0.1635]	-0.0265 (0.01)	-0.0235 (0.01)
ν_{132}[0.1807]	0.0017 (0.00)	0.0014 (0.00)	ν_{178}[0.1813]	-0.0011 (0.00)	-0.0010 (0.00)	ν_{224}[0.1814]	0.0003 (0.00)	0.0003 (0.00)
ν_{145}[0.2003]	-0.1978 (0.49)	-0.1422 (0.25)	ν_{195}[0.2017]	-0.1648 (0.33)	-0.1380 (0.23)	ν_{245}[0.2024]	-0.1430 (0.25)	-0.1299 (0.21)
ν_{161}[0.3938]	-0.0038 (0.00)	-0.0032 (0.00)	ν_{219}[0.3941]	-0.0029 (0.00)	-0.0027 (0.00)	ν_{275}[0.3941]	-0.0025 (0.00)	-0.0023 (0.00)
ν_{174}[0.3963]	0.0071 (0.00)	0.0067 (0.00)	ν_{234}[0.3959]	-0.0062 (0.00)	-0.0061 (0.00)	ν_{294}[0.3958]	0.0048 (0.00)	0.0047 (0.00)

Table SI5: Jahn-Teller (JT) coupling parameters (λ) of T_2 state of CPP derived at TD-B3LYP/6-311G(d) level of theory. All values are in eV. The coupling strength ($\lambda^2/2\omega^2$) is given in the paranthesis.

[6]CPP		[8]CPP		[10]CPP	
e_g mode	$\lambda^{(T_2)}$	e_2 mode	$\lambda^{(T_2)}$	e_{2g} mode	$\lambda^{(T_2)}$
ν_1 [0.0055]	0.0160 (4.23)	ν_1 [0.0031]	0.0080 (3.33)	ν_1 [0.0020]	0.0055 (3.78)
ν_8 [0.0160]	0.0221 (0.95)	ν_3 [0.0046]	0.0158 (5.90)	ν_8 [0.0075]	0.0231 (4.74)
ν_{15} [0.0302]	0.0040 (0.00)	ν_{13} [0.0142]	0.0244 (1.48)	ν_{19} [0.0147]	0.0221 (1.13)
ν_{22} [0.0302]	0.0101 (0.06)	ν_{25} [0.0370]	0.0005 (0.00)	ν_{33} [0.0348]	0.0081 (0.03)
ν_{31} [0.0558]	0.0165 (0.04)	ν_{30} [0.0427]	0.0060 (0.01)	ν_{38} [0.0412]	0.0080 (0.02)
ν_{33} [0.0597]	0.0098 (0.01)	ν_{37} [0.0500]	0.0130 (0.03)	ν_{42} [0.0494]	0.0059 (0.01)
ν_{41} [0.0730]	0.0118 (0.01)	ν_{43} [0.0555]	0.0135 (0.03)	ν_{54} [0.0532]	0.0142 (0.04)
ν_{44} [0.0795]	0.0110 (0.01)	ν_{54} [0.0711]	0.0096 (0.01)	ν_{68} [0.0695]	0.0075 (0.01)
ν_{50} [0.0859]	0.0149 (0.02)	ν_{63} [0.0807]	0.0073 (0.00)	ν_{81} [0.0813]	0.0050 (0.00)
ν_{56} [0.0932]	0.0099 (0.01)	ν_{70} [0.0900]	0.0118 (0.01)	ν_{90} [0.0921]	0.0083 (0.00)
ν_{62} [0.0995]	0.0089 (0.00)	ν_{78} [0.0954]	0.0058 (0.00)	ν_{100}[0.0971]	0.0121 (0.01)
ν_{70} [0.1065]	0.0304 (0.04)	ν_{88} [0.1018]	0.0122 (0.01)	ν_{111}[0.1028]	0.0129 (0.01)
ν_{74} [0.1178]	0.0095 (0.00)	ν_{94} [0.1057]	0.0193 (0.02)	ν_{118}[0.1049]	0.0144 (0.01)
ν_{80} [0.1190]	0.0027 (0.00)	ν_{102}[0.1185]	0.0089 (0.00)	ν_{133}[0.1189]	0.0062 (0.00)
ν_{89} [0.1266]	0.0347 (0.04)	ν_{110}[0.1194]	0.0080 (0.00)	ν_{140}[0.1195]	0.0028 (0.00)
ν_{92} [0.1290]	0.0141 (0.01)	ν_{119}[0.1266]	0.0246 (0.02)	ν_{151}[0.1267]	0.0189 (0.01)
ν_{98} [0.1417]	0.0122 (0.00)	ν_{126}[0.1306]	0.0162 (0.01)	ν_{160}[0.1315]	0.0140 (0.01)
ν_{104}[0.1511]	0.0336 (0.02)	ν_{134}[0.1419]	0.0081 (0.00)	ν_{170}[0.1420]	0.0056 (0.00)
ν_{112}[0.1522]	0.0503 (0.05)	ν_{142}[0.1516]	0.0371 (0.03)	ν_{180}[0.1515]	0.0378 (0.03)
ν_{116}[0.1602]	0.0219 (0.01)	ν_{147}[0.1591]	0.0363 (0.03)	ν_{190}[0.1598]	0.0328 (0.02)
ν_{125}[0.1672]	0.0008 (0.00)	ν_{155}[0.1611]	0.0301 (0.02)	ν_{197}[0.1616]	0.0283 (0.02)
ν_{127}[0.1761]	0.0044 (0.00)	ν_{167}[0.1673]	0.0017 (0.00)	ν_{208}[0.1667]	0.0031 (0.00)
ν_{136}[0.1911]	0.0415 (0.02)	ν_{174}[0.1775]	0.0027 (0.00)	ν_{220}[0.1786]	0.0016 (0.00)
ν_{142}[0.1969]	0.0082 (0.00)	ν_{182}[0.1910]	0.0301 (0.01)	ν_{228}[0.1907]	0.0231 (0.01)
ν_{148}[0.2027]	0.0738 (0.07)	ν_{190}[0.1966]	0.0041 (0.00)	ν_{238}[0.1961]	0.0024 (0.00)
ν_{153}[0.3916]	0.0030 (0.00)	ν_{198}[0.2033]	0.0830 (0.08)	ν_{248}[0.2036]	0.0800 (0.08)
ν_{157}[0.3934]	0.0001 (0.00)	ν_{209}[0.3920]	0.0019 (0.00)	ν_{263}[0.3921]	0.0013 (0.00)
ν_{165}[0.3943]	0.0025 (0.00)	ν_{211}[0.3932]	0.0003 (0.00)	ν_{267}[0.3932]	0.0004 (0.00)
ν_{169}[0.3961]	0.0039 (0.00)	ν_{225}[0.3944]	0.0021 (0.00)	ν_{281}[0.3944]	0.0018 (0.00)
		ν_{230}[0.3957]	0.0038 (0.00)	ν_{290}[0.3956]	0.0036 (0.00)

Table SI6: Linear interstate (or pseudo-Jahn-Teller, PJT) coupling parameters (λ') associated with T_1-T_2 states of CPP derived at TD-B3LYP/6-311G(d) level of theory. All values are in eV.

[6]CPP		[8]CPP		[10]CPP	
e_u mode	$\lambda'_{T_1-T_2}$	e_1 mode	$\lambda'_{T_1-T_2}$	e_{1u} mode	$\lambda'_{T_1-T_2}$
ν_3 [0.0070]	0.0269 (7.38)	ν_7 [0.0092]	0.0335 (6.63)	ν_{12} [0.0104]	0.0338 (5.28)
ν_{10} [0.0186]	0.0224 (0.73)	ν_{16}[0.0187]	0.0189 (0.51)	ν_{23} [0.0195]	0.0077 (0.08)
ν_{17} [0.0360]	0.0100 (0.04)	ν_{23}[0.0281]	0.0137 (0.12)	ν_{26} [0.0230]	0.0123 (0.14)
ν_{20} [0.0411]		ν_{28}[0.0416]	0.0084 (0.02)	ν_{36} [0.0406]	0.0055 (0.01)
ν_{24} [0.0480]		ν_{32}[0.0490]		ν_{44} [0.0502]	
ν_{28} [0.0541]	0.0058 (0.01)	ν_{40}[0.0527]	0.0117 (0.02)	ν_{52} [0.0527]	0.0054 (0.01)
ν_{37} [0.0692]	0.0206 (0.04)	ν_{51}[0.0670]	0.0152 (0.03)	ν_{65} [0.0659]	0.0085 (0.01)
ν_{47} [0.0809]		ν_{65}[0.0815]		ν_{83} [0.0818]	
ν_{52} [0.0905]		ν_{75}[0.0929]		ν_{97} [0.0941]	
ν_{58} [0.0980]		ν_{80}[0.0995]	0.0173 (0.02)	ν_{102}[0.1001]	0.0172 (0.01)
ν_{64} [0.0995]	0.0098 (0.00)	ν_{83}[0.1015]	0.0054 (0.00)	ν_{106}[0.1025]	
ν_{68} [0.1036]	0.0298 (0.04)	ν_{92}[0.1032]	0.0215 (0.02)	ν_{116}[0.1031]	0.0194 (0.02)
ν_{77} [0.1179]		ν_{104}[0.1186]		ν_{129}[0.1188]	
ν_{83} [0.1191]		ν_{112}[0.1195]		ν_{142}[0.1198]	
ν_{86} [0.1259]	0.0193 (0.01)	ν_{116}[0.1262]	0.0136 (0.01)	ν_{147}[0.1263]	0.0080 (0.00)
ν_{94} [0.1315]	0.0033 (0.00)	ν_{128}[0.1323]	0.0089 (0.00)	ν_{162}[0.1327]	0.0051 (0.00)
ν_{101}[0.1418]		ν_{136}[0.1421]	0.0089 (0.00)	ν_{172}[0.1421]	0.0041 (0.00)
ν_{107}[0.1516]	0.0546 (0.06)	ν_{145}[0.1518]	0.0490 (0.05)	ν_{183}[0.1516]	0.0435 (0.04)
ν_{109}[0.1574]	0.0474 (0.05)	ν_{152}[0.1593]	0.0420 (0.03)	ν_{192}[0.1602]	0.0374 (0.03)
ν_{118}[0.1610]		ν_{160}[0.1620]	0.0148 (0.00)	ν_{202}[0.1625]	0.0149 (0.00)
ν_{122}[0.1661]		ν_{164}[0.1659]		ν_{206}[0.1656]	
ν_{130}[0.1782]		ν_{176}[0.1798]		ν_{222}[0.1805]	
ν_{134}[0.1890]	0.0243 (0.01)	ν_{180}[0.1893]	0.0159 (0.00)	ν_{226}[0.1894]	0.0113 (0.00)
ν_{140}[0.1942]		ν_{188}[0.1943]		ν_{236}[0.1943]	
ν_{146}[0.2008]	0.0915 (0.10)	ν_{196}[0.2022]	0.0860 (0.09)	ν_{246}[0.2028]	0.0767 (0.07)
ν_{155}[0.3916]		ν_{207}[0.3919]	0.0024 (0.00)	ν_{259}[0.3920]	
ν_{159}[0.3934]		ν_{215}[0.3934]	0.0031 (0.00)	ν_{271}[0.3934]	
ν_{167}[0.3943]		ν_{221}[0.3943]	0.0011 (0.00)	ν_{276}[0.3943]	
ν_{172}[0.3962]	0.0067 (0.00)	ν_{232}[0.3959]	0.0072 (0.00)	ν_{292}[0.3957]	0.0029 (0.00)

Table SI7: MCTDH details of normal mode[a] combination, size of the primitive and single particle bases used in the T_1-T_2 vibronic dynamics of CPP.

	Normal modes	Primitive basis [b]	SPF basis [c] $[T_1, T_{2x}, T_{2y}]$
[6]CPP	$(\nu_{1y}, \nu_5, \nu_{8x}, \nu_{8y}, \nu_{136x})$	(6, 8, 4, 5, 5)	[6, 4, 4]
	$(\nu_{1x}, \nu_{10x}, \nu_{14}, \nu_{67}, \nu_{104x})$	(6, 4, 6, 5, 5)	[4, 5, 5]
	$(\nu_{3y}, \nu_{19}, \nu_{36}, \nu_{70x}\ \nu_{111}, \nu_{145})$	(4, 6, 4, 6, 5, 6)	[5, 6, 6]
	$(\nu_{70y}, \nu_{89y}, \nu_{104x}\ \nu_{112x}, \nu_{148x})$	(5, 5, 4, 5, 4)	[6, 5, 5]
	$(\nu_{10y}, \nu_{89x}, \nu_{136y}, \nu_{146y})$	(4, 5, 4, 4)	[4, 6, 6]
	$(\nu_{3x}, \nu_{112y}, \nu_{146x}, \nu_{148y})$	(4, 4, 4, 4)	[4, 6, 6]
[8]CPP	$(\nu_{1y}, \nu_{3y}, \nu_{10}, \nu_{13x}, \nu_{198x})$	(5, 4, 8, 5, 4)	[6, 5, 5]
	$(\nu_{1x}, \nu_{19}, \nu_{23x}, \nu_{144}, \nu_{155y})$	(5, 5, 4, 5, 4)	[4, 5, 5]
	$(\nu_{3x}, \nu_{16y}, \nu_{27}, \nu_{50}, \nu_{154}, \nu_{195})$	(4, 6, 5, 4, 5, 4)	[6, 4, 4]
	$(\nu_{7x}, \nu_{147yx}, \nu_{155x}, \nu_{182x})$	(4, 6, 4, 4)	[4, 6, 6]
	$(\nu_{13y}, \nu_{23y}, \nu_{147x}, \nu_{196y}, \nu_{198y})$	(5, 4, 6, 4, 4)	[6, 4, 4]
	$(\nu_{7y}, \nu_{16x}, \nu_{182y}, \nu_{196y})$	(6, 4, 4, 4)	[6, 5, 5]
[10]CPP	$(\nu_{8x}, \nu_{14}, \nu_{19x}, \nu_{19y}, \nu_{248x})$	(5, 8, 4, 4, 5)	[6, 5, 5]
	$(\nu_{1x}, \nu_{21}, \nu_{26x}, \nu_{180y}, \nu_{182})$	(6, 6, 4, 5, 5)	[5, 6, 6]
	$(\nu_{1y}, \nu_{23y}, \nu_{35}, \nu_{105}, \nu_{194}, \nu_{245})$	(6, 4, 6, 6, 5, 6)	[4, 5, 5]
	$(\nu_{12x}, \nu_{151yx}, \nu_{180x}, \nu_{190x})$	(5, 5, 5, 4)	[6, 4, 4]
	$(\nu_{26y}, \nu_{151x}, \nu_{246y}, \nu_{248y})$	(4, 5, 4, 5)	[6, 5, 5]
	$(\nu_{8y}, \nu_{12y}, \nu_{23x}, \nu_{190y}, \nu_{246x})$	(5, 5, 4, 4, 4)	[5, 6, 6]

[a] The components of degenerate vibrational mode are described with the notation of x and y for brevity. Note that ν_{1x} corresponds to ν_1 (cf. SI1-SI3) and ν_{1y} corresponds to ν_2 (cf., SI1-SI3). This description is applicable for all other relevant degenerate vibrational modes. [b] The primitive basis for each particle is the product of the one-dimensional bases; for instance, the primitive basis for particle 1 of [6]CPP (with ν_{1y}, ν_5, ν_{8x}, ν_{8y}, ν_{136x}) contains $6 \times 8 \times 4 \times 5 \times 5 = 4800$ functions. The full primitive basis consists of a total of 4.8922×10^{19} functions. Similarly, a full primitive basis of i1.7395×10^{19} and 9.5551×10^{19} functions are used in the dynamics of [8] and [10]CPP, respectively. [c] The SPF basis represents the number of single-particle functions.

Table SI8: TD-B3LYP/6-31G(d) singlet and triplet vertical excitation energies of cyclic- (CPP) and linear- (OPP) polyphenylenes. All values are in eV.

[n]CPP (Point group)	S_1	T_1	T_2	T_3
6(D_{3d})	2.5147	1.9533	2.4992	3.4301
8(D_{4d})	2.8780	2.2904	2.5573	3.1097
10(D_{5d})	3.0883	2.4603	2.6118	2.9831
12(C_2)	3.1825	2.5190	2.6211	2.8865
14(C_1)	3.2479	2.5813	2.6531	2.8520
16(D_{8d})	3.2840	2.6094	2.6639	2.8186
18(C_i)	3.3110	2.6311	2.6749	2.7956
20(C_1)	3.0802	2.6459	2.6805	2.7795

[n]OPP (Point group)	S_1	T_1	T_2	T_3
6(C_2)	3.7450	2.8101	3.0725	3.3947
8(C_2)	3.6067	2.7625	2.9238	3.1473
10(C_2)	3.5455	2.7490	2.8516	3.0198
12(C_2)	3.5130	2.7431	2.8195	2.9359
14(C_2)	3.4568	2.7117	2.7737	2.8677
16(C_2)	3.4466	2.7138	2.7585	2.8326
18(C_2)	3.4267	2.7043	2.7403	2.8016
20(C_2)	3.4271	2.7111	2.7876	2.8507

Table SI9: Ground-state (S_0) equilibrium geometry of [6]CPP optimized at TD-B3LYP/6-31G(d) level of theory.

Atom	Coordinates (Angstroms)		
	X	Y	Z
C	-0.693929	3.753083	1.262196
C	-0.695125	4.444235	-1.022594
C	0.693929	3.753083	1.262196
H	-1.202970	3.409160	2.155492
C	0.695125	4.444235	-1.022594
H	-1.217246	4.730178	-1.930455
C	1.420636	3.941620	0.074995
H	1.202970	3.409160	2.155492
H	1.217246	4.730178	-1.930455
C	-3.501258	2.824114	1.022594
C	-2.903300	2.477502	-1.262196
C	-4.196383	1.620121	1.022594
H	-3.487831	3.419255	1.930455
C	-3.597230	1.275581	-1.262196
H	-2.350934	2.746383	-2.155492
C	-4.123861	0.740503	-0.074995
H	-4.705077	1.310923	1.930455
H	-3.553904	0.662777	-2.155492
C	-4.123861	-0.740503	0.074995
C	-4.196383	-1.620121	-1.022594
C	-3.597230	-1.275581	1.262196
C	-3.501258	-2.824114	-1.022594
H	-4.705077	-1.310923	-1.930455
C	-2.903300	-2.477502	1.262196
H	-3.553904	-0.662777	2.155492
C	-2.703225	-3.201117	0.074995
H	-3.487831	-3.419255	-1.930455
H	-2.350934	-2.746383	2.155492
C	-1.420636	-3.941620	-0.074995
C	-0.695125	-4.444235	1.022594
C	-0.693929	-3.753083	-1.262196
C	0.695125	-4.444235	1.022594
H	-1.217246	-4.730178	1.930455
C	0.693929	-3.753083	-1.262196
H	-1.202970	-3.409160	-2.155492
C	1.420636	-3.941620	-0.074995
H	1.217246	-4.730178	1.930455
H	1.202970	-3.409160	-2.155492
C	2.703225	-3.201117	0.074995
C	3.501258	-2.824114	-1.022594
C	2.903300	-2.477502	1.262196
C	4.196383	-1.620121	-1.022594
H	3.487831	-3.419255	-1.930455
C	3.597230	-1.275581	1.262196
H	2.350934	-2.746383	2.155492
C	4.123861	-0.740503	0.074995
H	4.705077	-1.310923	-1.930455
H	3.553904	-0.662777	2.155492
C	4.123861	0.740503	-0.074995
C	4.196383	1.620121	1.022594
C	3.597230	1.275581	-1.262196
C	3.501258	2.824114	1.022594
H	4.705077	1.310923	1.930455
C	2.903300	2.477502	-1.262196
H	3.553904	0.662777	-2.155492
C	2.703225	3.201117	-0.074995
H	3.487831	3.419255	1.930455
H	2.350934	2.746383	-2.155492
C	-2.703225	3.201117	-0.074995
C	-1.420636	3.941620	0.074995

Table SI10: Ground-state (S_0) equilibrium geometry of [8]CPP optimized at TD-B3LYP/6-31G(d) level of theory.

Atom	Coordinates (Angstroms)		
	X	Y	Z
C	-0.693877	5.118263	1.232646
C	0.693877	5.118263	1.232646
C	1.422328	5.368416	0.059141
C	0.695017	5.847245	-1.045112
C	-0.695017	5.847245	-1.045112
C	-1.422328	5.368416	0.059141
H	-1.209333	4.763645	2.118407
H	1.209333	4.763645	2.118407
H	1.220489	6.150040	-1.945439
H	-1.220489	6.150040	-1.945439
C	2.790306	4.801781	-0.059141
C	3.643175	4.626078	1.045112
C	3.128513	4.109804	-1.232646
C	4.626078	3.643175	1.045112
H	3.485719	5.211751	1.945439
C	4.109804	3.128513	-1.232646
H	2.513278	4.223533	-2.118407
C	4.801781	2.790306	-0.059141
H	5.211751	3.485719	1.945439
H	4.223533	2.513278	-2.118407
C	-2.790306	4.801781	-0.059141
C	-3.128513	4.109804	-1.232646
C	-3.643175	4.626078	1.045112
C	-4.109804	3.128513	-1.232646
H	-2.513278	4.223533	-2.118407
C	-4.626078	3.643175	1.045112
H	-3.485719	5.211751	1.945439
C	-4.801781	2.790306	-0.059141
H	-4.223533	2.513278	-2.118407
H	-5.211751	3.485719	1.945439
C	5.368416	1.422328	0.059141
C	5.847245	0.695017	-1.045112
C	5.118263	0.693877	1.232646
C	5.847245	-0.695017	-1.045112
H	6.150040	1.220489	-1.945439
C	5.118263	-0.693877	1.232646
H	4.763645	1.209333	2.118407
C	5.368416	-1.422328	0.059141
H	6.150040	-1.220489	-1.945439
H	4.763645	-1.209333	2.118407
C	4.801781	-2.790306	-0.059141
C	4.626078	-3.643175	1.045112
C	4.109804	-3.128513	-1.232646
C	3.643175	-4.626078	1.045112
H	5.211751	-3.485719	1.945439
C	3.128513	-4.109804	-1.232646
H	4.223533	-2.513278	-2.118407
C	2.790306	-4.801781	-0.059141
H	3.485719	-5.211751	1.945439
H	2.513278	-4.223533	-2.118407

conti.

Table SI10: Ground-state (S_0) equilibrium geometry of [8]CPP optimized at TD-B3LYP/6-31G(d) level of theory.

Atom	Coordinates (Angstroms)		
	X	Y	Z
conti.			
C	4.801781	-2.790306	-0.059141
C	4.626078	-3.643175	1.045112
C	4.109804	-3.128513	-1.232646
C	3.643175	-4.626078	1.045112
H	5.211751	-3.485719	1.945439
C	3.128513	-4.109804	-1.232646
H	4.223533	-2.513278	-2.118407
C	2.790306	-4.801781	-0.059141
H	3.485719	-5.211751	1.945439
H	2.513278	-4.223533	-2.118407
C	1.422328	-5.368416	0.059141
C	0.695017	-5.847245	-1.045112
C	0.693877	-5.118263	1.232646
C	-0.695017	-5.847245	-1.045112
H	1.220489	-6.150040	-1.945439
C	-0.693877	-5.118263	1.232646
H	1.209333	-4.763645	2.118407
C	-1.422328	-5.368416	0.059141
H	-1.220489	-6.150040	-1.945439
H	-1.209333	-4.763645	2.118407
C	-2.790306	-4.801781	-0.059141
C	-3.643175	-4.626078	1.045112
C	-3.128513	-4.109804	-1.232646
C	-4.626078	-3.643175	1.045112
H	-3.485719	-5.211751	1.945439
C	-4.109804	-3.128513	-1.232646
H	-2.513278	-4.223533	-2.118407
C	-4.801781	-2.790306	-0.059141
H	-5.211751	-3.485719	1.945439
H	-4.223533	-2.513278	-2.118407
C	-5.368416	-1.422328	0.059141
C	-5.847245	-0.695017	-1.045112
C	-5.118263	-0.693877	1.232646
C	-5.847245	0.695017	-1.045112
H	-6.150040	-1.220489	-1.945439
C	-5.118263	0.693877	1.232646
H	-4.763645	-1.209333	2.118407
C	-5.368416	1.422328	0.059141
H	-6.150040	1.220489	-1.945439
H	-4.763645	1.209333	2.118407

Table SI11: Ground-state (S_0) equilibrium geometry of [10]CPP optimized at TD-B3LYP/6-31G(d) level of theory.

Atom	Coordinates (Angstroms)		
	X	Y	Z
C	4.820070	5.451896	1.057195
C	3.695578	6.268887	1.057195
C	2.830869	6.316336	-0.049439
C	3.249200	5.652869	-1.212719
C	4.372140	4.837005	-1.212719
C	5.132406	4.644171	-0.049439
H	5.433276	5.398451	1.951323
H	3.455257	6.835566	1.951323
H	2.615273	5.664603	-2.092685
H	4.579193	4.237731	-2.092685
C	1.422428	6.773966	0.049439
C	0.694015	6.483099	1.212719
C	0.694974	7.243842	-1.057195
C	-0.694015	6.483099	1.212719
H	1.213770	6.119979	2.092685
C	-0.694974	7.243842	-1.057195
H	1.222483	7.561038	-1.951323
C	-1.422428	6.773966	0.049439
H	-1.213770	6.119979	2.092685
H	-1.222483	7.561038	-1.951323
C	6.002870	3.446080	0.049439
C	6.674545	2.899430	-1.057195
C	5.951331	2.663436	1.212719
C	7.104062	1.577511	-1.057195
H	6.813207	3.499140	-1.951323
C	6.380256	1.343340	1.212719
H	5.445370	3.045541	2.092685
H	7.568743	1.173839	-1.951323
H	6.195521	0.736814	2.092685
C	-2.830869	6.316336	-0.049439
C	-3.249200	5.652869	-1.212719
C	-3.695578	6.268887	1.057195
C	-4.372140	4.837005	-1.212719
H	-2.615273	5.664603	-2.092685
H	-4.820070	5.451896	1.057195
H	-3.455257	6.835566	1.951323
C	-5.132406	4.644171	-0.049439
H	-4.579193	4.237731	-2.092685
H	-5.433276	5.398451	1.951323
C	-6.002870	3.446080	0.049439
C	-5.951331	2.663436	1.212719
C	-6.674545	2.899430	-1.057195
C	-6.380256	1.343340	1.212719
H	-5.445370	3.045541	2.092685
C	-7.104062	1.577511	-1.057195
H	-6.813207	3.499140	-1.951323
C	-6.881979	0.740461	0.049439
H	-6.195521	0.736814	2.092685
H	-7.568743	1.173839	-1.951323
C	-6.881979	-0.740461	-0.049439
C	-6.380256	-1.343340	-1.212719
C	-7.104062	-1.577511	1.057195
C	-5.951331	-2.663436	-1.212719
H	-6.195521	-0.736814	-2.092685
C	-6.674545	-2.899430	1.057195
H	-7.568743	-1.173839	1.951323
C	-6.002870	-3.446080	-0.049439
H	-5.445370	-3.045541	-2.092685
H	-6.813207	-3.499140	1.951323
C	-5.132406	-4.644171	0.049439

conti.

Table SI11: Ground-state (S_0) equilibrium geometry of [10]CPP optimized at TD-B3LYP/6-31G(d) level of theory.

Atom	Coordinates (Angstroms)		
	X	Y	Z
conti.			
C	-4.372140	-4.837005	1.212719
C	-4.820070	-5.451896	-1.057195
C	-3.249200	-5.652869	1.212719
H	-4.579193	-4.237731	2.092685
C	-3.695578	-6.268887	-1.057195
H	-5.433276	-5.398451	-1.951323
C	-2.830869	-6.316336	0.049439
H	-2.615273	-5.664603	2.092685
H	-3.455257	-6.835566	-1.951323
C	-1.422428	-6.773966	-0.049439
C	-0.694015	-6.483099	-1.212719
C	-0.694974	-7.243842	1.057195
C	0.694015	-6.483099	-1.212719
H	-1.213770	-6.119979	-2.092685
C	0.694974	-7.243842	1.057195
H	-1.222483	-7.561038	1.951323
C	1.422428	-6.773966	-0.049439
H	1.213770	-6.119979	-2.092685
H	1.222483	-7.561038	1.951323
C	2.830869	-6.316336	0.049439
C	3.249200	-5.652869	1.212719
C	3.695578	-6.268887	-1.057195
C	4.372140	-4.837005	1.212719
H	2.615273	-5.664603	2.092685
C	4.820070	-5.451896	-1.057195
H	3.455257	-6.835566	-1.951323
C	5.132406	-4.644171	0.049439
H	4.579193	-4.237731	2.092685
H	5.433276	-5.398451	-1.951323
C	6.002870	-3.446080	-0.049439
C	5.951331	-2.663436	-1.212719
C	6.674545	-2.899430	1.057195
C	6.380256	-1.343340	-1.212719
H	5.445370	-3.045541	-2.092685
C	7.104062	-1.577511	1.057195
H	6.813207	-3.499140	1.951323
C	6.881979	-0.740461	-0.049439
H	6.195521	-0.736814	-2.092685
H	7.568743	-1.173839	1.951323
C	6.881979	0.740461	0.049439