Supporting information for:

Origin of the Size-Dependent Fluorescence Blueshift in [*n*]Cycloparaphenylenes

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The presented supporting information reports additional details on the calculations performed for the explanation of the origin of the fluorescence blueshift in [*n*]cycloparaphenylenes (CPPs). First, we present the linear regression curves obtained for S_0, S_1, S_2 relative energies defined with respect to S_2 optimized geometry as well as the $S_1 \rightarrow S_0$ and $S_2 \rightarrow S_0$ transition energies as a function of ovality and dihedral angles for [8] and [10]CPP. Second, we present the HOMO and LUMO orbital energies of a terphenyl model system as function of the dihedral and bending angles for adjacent phenyl units. Third, we provide the Cartesian coordinates for the ground (S_0) and excited state (S_1 and S_2) optimized geometries for [8] and [10]CPP. Finally, we show the convergence of the band position in the simulated fluorescence spectra of [*n*]CPPs with respect to the number of employed molecular dynamics (MD) trajectory sampling points.

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[*n*]CPP geometrical deformation

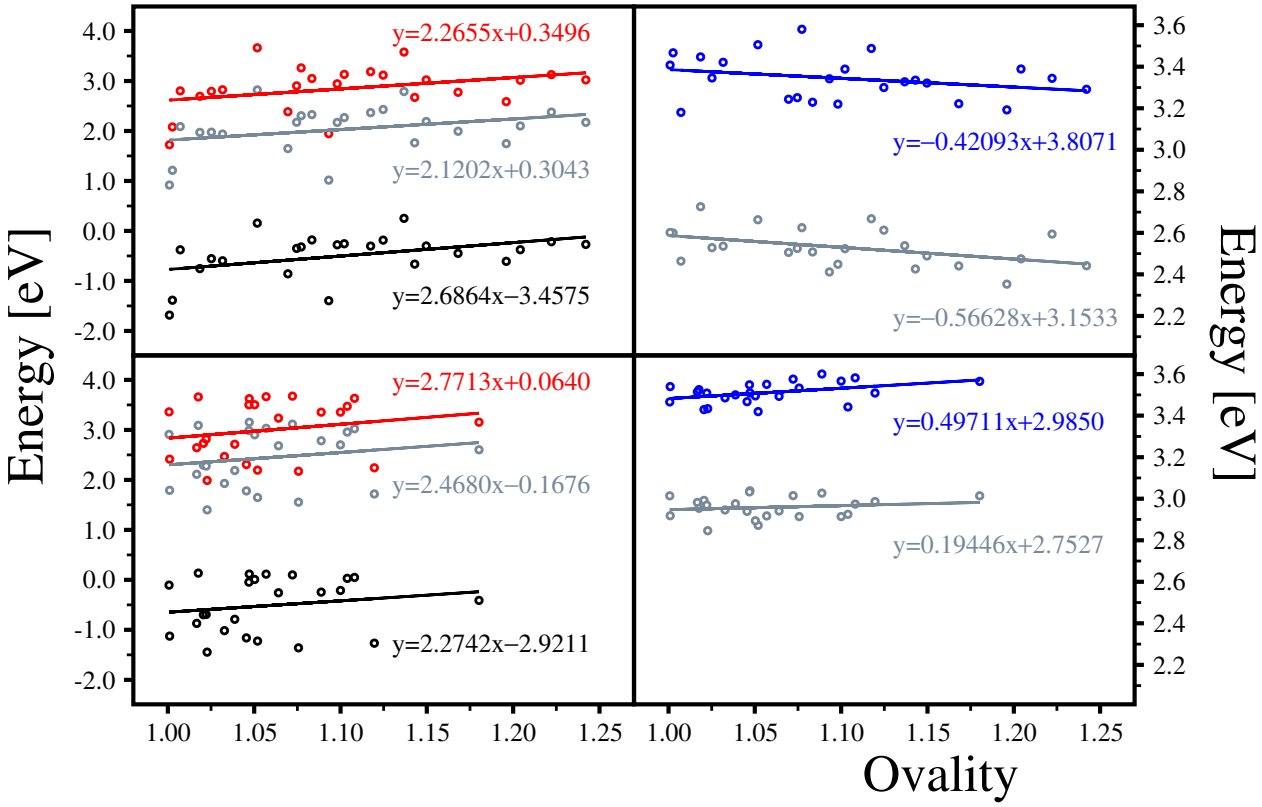

Figure S1: Electronic state energies of S_0 (black), S_1 (grey) and S_2 (red) states of 24 sampling geometries relative to S_2 optimized energy (left panel) and corresponding transition energies (right panel) as a function of ovality. Top: [8]CPP, bottom: [10]CPP.

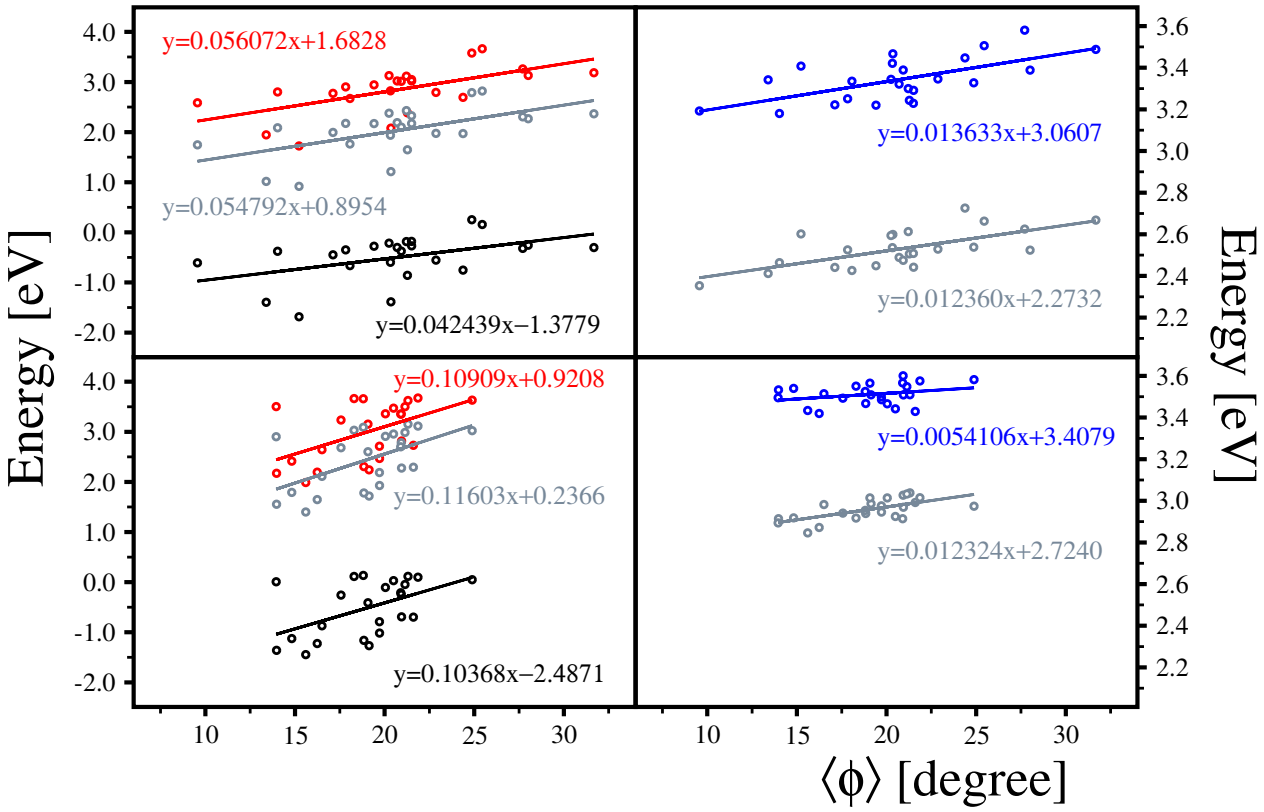

Figure S2: Electronic state energies of S_0 (black), S_1 (grey) and S_2 (red) states of 24 sampling geometries relative to S_2 optimized energy (left panel) and corresponding transition energies (right panel) as a function of the average torsional angles. Top: [8]CPP, bottom: [10]CPP.

Terphenyl HOMO and LUMO orbital energies

A discussion of the slightly different response to HOMO and LUMO levels to bending and torsional effects in CPP was recently given in ref.[S1] Figure S3 shows the quantitative dependence of ΔE_{HL} on bending and torsional deformations for a terphenyl model system. This plot indicates the lowering of ΔE_{HL} with increasing bending between of PP units, and increasing planarity measured by the dihedral angles between adjacent PP units. Figures S4a and S4b displays the underlying changes individually for the HOMO and the LUMO levels, respectively. In the case of the HOMO, we find that particularly the bending deformation brings together the antibonding lobes on adjacent PP units, raising its energy with increasing bending angle, while the torsional deformation is less affecting the HOMO energy. In the case of the LUMO, we find an important $\pi-$bond stabilization between PP units (stronger π bonding), which is lowered more dramatically with increasing

planarity as opposed to the bending deformation, similar as in the case of twisted ethylene.

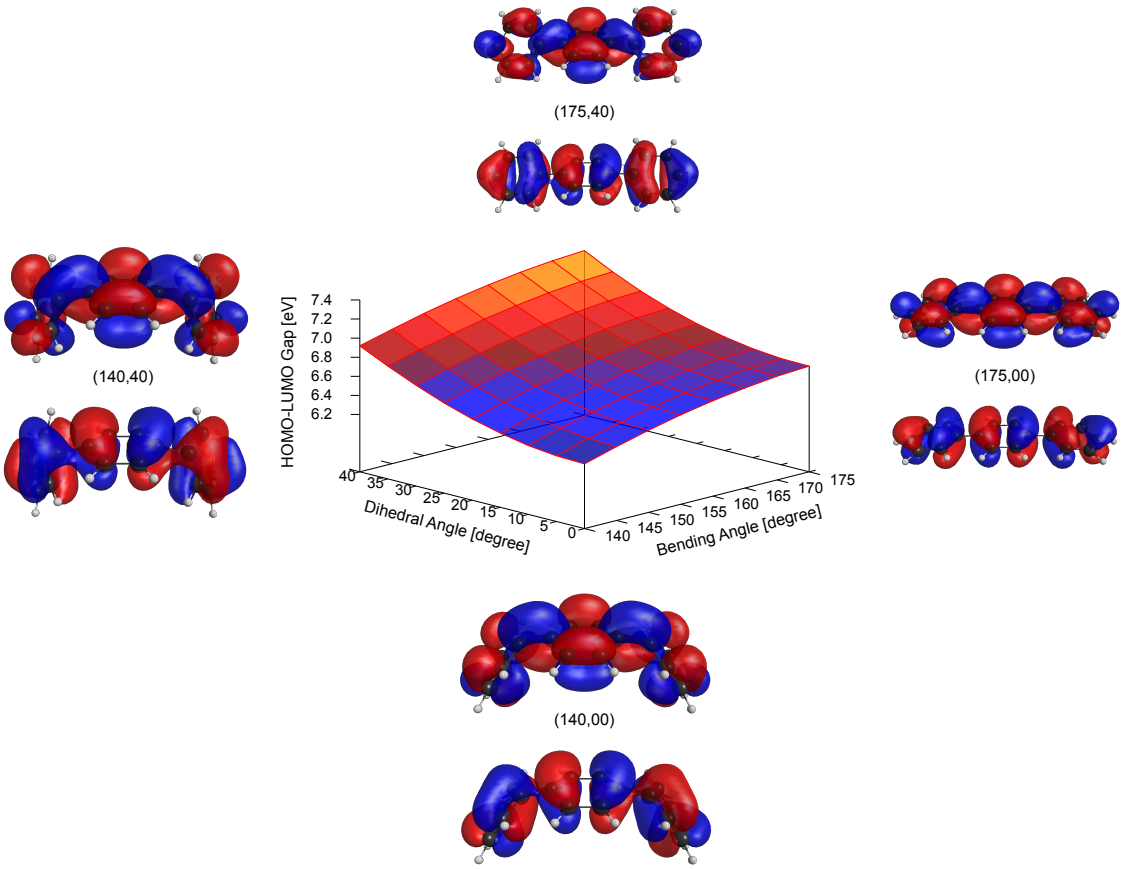

Figure S3: Terphenyl HOMO-LUMO gap and frontier molecular orbitals as a function of the dihedral and bending angles for adjacent phenyl units.

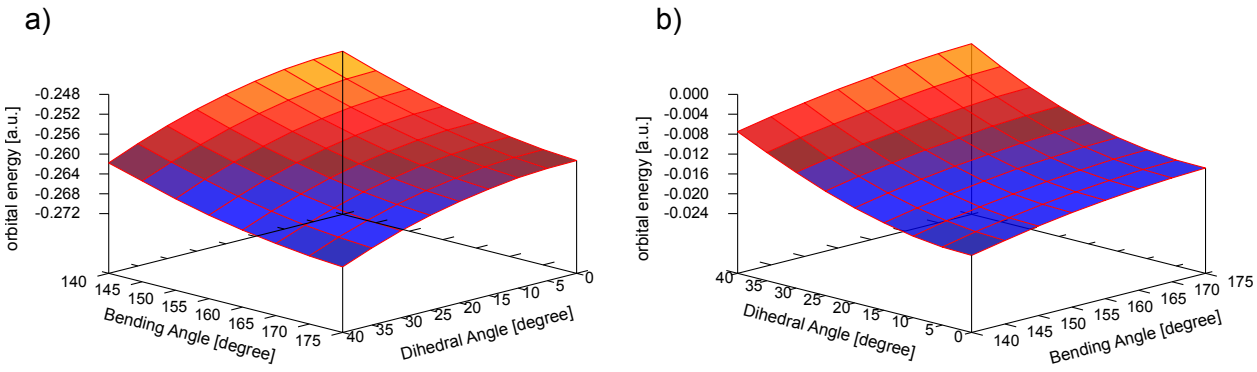

Figure S4: (a): Terphenyl HOMO one-electron orbital energies as function of the dihedral and bending angles for adjacent phenyl units. (b): Terphenyl LUMO one-electron orbital energies as function of the dihedral and bending angles for adjacent phenyl units.

Optimized geometries

Table S1: Cartesian coordinates of ground state (S_0) optimized geometries (given in Å) of [8] and [10]CPP at the CAM-B3LYP/def-SV(P) level of theory.

	[8]CPP				[10]CPP		
C	-0.0199242435	5.1721588564	-1.2304010095	C	-4.9102086986	-5.3630633062	-1.0627376745
C	-1.3957648032	4.9812537243	-1.2306219245	C	-5.8400568955	-4.3289581828	-1.0613176271
C	-2.1487257936	5.1228120546	-0.0574873321	C	-5.9887033994	-3.4874199854	0.0512335000
C	-1.4948588460	5.6856741028	1.0499387467	C	-5.2976442796	-3.8440979983	1.2164619159
C	-0.1171203498	5.8770068655	1.0501238524	C	-4.3689655915	-4.8771713695	1.2150915717
C	0.6658279328	5.5135384550	-0.0569686684	C	-4.0881534649	-5.6008739756	0.0488957531
H	0.5426753356	4.8992348784	-2.1259342557	H	-4.7766054765	-5.9551770925	-1.9719402951
H	-1.8629798981	4.5659184751	-2.1262988611	H	-6.4157641573	-4.1315495002	-1.9694274312
H	-2.0584316543	5.8972448938	1.9626066229	H	-5.3880487034	-3.2227786233	2.1103923424
H	0.3667058693	6.2344635885	1.9631084811	H	-3.7595187559	-5.0345074341	2.1079095273
C	-3.4287074641	4.3709878354	0.0569846529	C	-6.5898549044	-2.1304157839	-0.0439235090
C	-4.2402010756	4.0741684883	-1.0494418502	C	-6.3879471840	-1.3805806841	-1.2098388607
C	-3.6700420681	3.6436088169	1.2300452130	C	-7.1163603635	-1.4539646616	1.0665496352
C	-5.0778211520	2.9634726272	-1.0486022901	C	-6.5319391783	0.0009002490	-1.2121219907
H	-4.1530559562	4.6693096902	-1.9624401810	H	-5.9853570368	-1.8664272719	-2.1015202646
C	-4.5061316280	2.5343916150	1.2308019937	C	-7.2609372228	-0.0707411479	1.0641470048
H	-3.0784006944	3.8488516268	2.1249261451	H	-7.3579048077	-2.0116008456	1.9752850423
C	-5.1397748444	2.1022336153	0.0581211651	C	-6.8846590607	0.6966437047	-0.0484388335
H	-5.6267222563	2.7144730759	-1.9607590878	H	-6.2373488888	0.5563057338	-2.1054245760
H	-4.5397733201	1.9100261143	2.1263268384	H	-7.6135021787	0.4270513665	1.9713645514
C	2.1022346681	5.1397661775	0.0580310961	C	-2.8018399330	-6.3412909497	-0.0462737282
C	2.5344557118	4.5061118245	1.2306820837	C	-2.1836779663	-6.9344639029	1.0645919451
C	2.9634148726	5.0778250427	-1.0487395132	C	-2.0350397665	-6.2198867323	-1.2124244126
C	3.6436751712	3.6700245100	1.2298589425	C	-0.8227839022	-7.2210399623	1.0625809332
H	1.9101381844	4.5397430460	2.1262405951	H	-2.7630161979	-7.1173912192	1.9734591998
C	4.0741121765	4.2402078398	-1.0496451933	C	-0.6758045377	-6.5059839429	-1.2144066666
H	2.7143653809	5.6267345518	-1.9608775666	H	-2.4765894137	-5.7704178824	-2.1047650574
C	4.3709931166	3.4287045379	0.0567581781	H	-0.3639313055	-7.6221107941	1.9701368626
H	3.8489639456	3.0783741889	2.1247233515	H	-0.0928030318	-6.2718164669	-2.1080440269
H	4.6692071118	4.1530717349	-1.9626746885	C	-6.5742544158	2.1481104504	0.0442296304
C	-5.5135453007	0.6658327038	-0.0569595987	C	-5.9722800471	2.6388797300	1.2101250590
C	-5.8770110710	-0.1171814843	1.0500870863	C	-6.5996692311	3.0020536816	-1.0686005061
C	-5.1721676413	-0.0198518206	-1.2304320110	C	-5.2756580459	3.8405260708	1.2109477680
C	-5.6856770004	-1.4949197428	1.0498208078	H	-5.9345626288	2.0114501097	2.1035287155

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Table S1 – *Continued from previous page*

	[8]CPP				**[10]CPP**		
H	-6.2344677657	0.3665894216	1.9631008738	C	-5.9024934722	4.2053424857	-1.0676767506
C	-4.9812629320	-1.3956922489	-1.2307352038	H	-7.1215208236	2.6920830510	-1.9778310762
H	-4.8992490353	0.5427987381	-2.1259346962	C	-5.1495101365	4.6076333128	0.0455103491
C	-5.1228165144	-2.1487220080	-0.0576443255	H	-4.7129668707	4.1185765349	2.1049713499
H	-5.8972474365	-2.0585460805	1.9624555837	H	-5.8924906311	4.8132919652	-1.9761623780
H	-4.5659303493	-1.8628543434	-2.1264410028	C	-4.0481850279	5.6025432296	-0.0469648585
C	-4.3709906328	-3.4287091172	0.0567536834	C	-3.2721266128	5.6516574211	-1.2123317695
C	-4.0741668153	-4.2401395632	-1.0497176055	C	-3.5710187480	6.3090148658	1.0672002900
C	-3.6436143708	-3.6701091796	1.2298027616	C	-2.0052051314	6.2211000852	-1.2103867400
C	-2.9634696621	-5.0777587909	-1.0489216119	H	-3.6061008516	5.1219163349	-2.1073975136
H	-4.6693047216	-4.1529431802	-1.9627131937	C	-2.3024944646	6.8788065452	1.0692022631
C	-2.5343962561	-4.5061968217	1.2305159657	H	-4.1770214619	6.3592470977	1.9756931590
H	-3.8488604113	-3.0785184530	2.1247163371	C	-1.4552694246	6.7673898061	-0.0434925631
C	-2.1022339639	-5.1397739355	0.0578007594	H	-1.3847997096	6.1205847964	-2.1038462713
H	-2.7144661913	-5.6266074901	-1.9611089539	H	-1.9406864376	7.3643439960	1.9794183717
H	-1.9100331627	-4.5398878793	2.1260405956	C	0.0203697153	6.9268775459	0.0499955917
C	-0.6658318646	-5.5135355363	-0.0572937992	C	0.6758056765	6.5060023686	1.2144022956
C	0.1171741391	-5.8770665269	1.0497374576	C	0.8227810397	7.2210416504	-1.0625906553
C	0.0198607618	-5.1720873605	-1.2307407821	C	2.0350393932	6.2199001051	1.2124181601
C	1.4949121320	-5.6857325047	1.0494922582	H	0.0928050534	6.2718456127	2.1080429462
H	-0.3666034508	-6.2345772576	1.9627265003	C	2.1836743706	6.9344605317	-1.0646034472
C	1.3957014752	-4.9811825742	-1.2310228505	H	0.3639313034	7.6221127483	-1.9701478738
H	-0.5427837154	-4.8991154625	-2.1262311271	C	2.8018367286	6.3412925311	0.0462640463
C	2.1487224607	-5.1228069524	-0.0579351251	H	2.4765923297	5.7704363719	2.1047598028
H	2.0585325503	-5.8973558129	1.9621184141	H	2.7630089262	7.1173796833	-1.9734748184
H	1.8628700469	-4.5657965619	-2.1267004680	C	4.0881467216	5.6008695692	-0.0489037650
C	3.4287098262	-4.3709898038	0.0565174841	C	4.3689521633	4.8771567148	-1.2150952419
C	4.2401493775	-4.0741014353	-1.0499298898	C	4.9102058335	5.3630641838	1.0627273462
C	3.6701016637	-3.6436833625	1.2296113419	C	5.2976304384	3.8440833716	-1.2164629167
C	5.0777697703	-2.9634054803	-1.0490623827	H	3.7595003741	5.0344866312	-2.1079108005
H	4.1529589184	-4.6691853900	-1.9629611944	C	5.8400557693	4.3289601691	1.0613096972
C	4.5061920428	-2.5344673147	1.2303965253	H	4.7766074989	5.9551809222	1.9719287330
H	3.0785039922	-3.8489802654	2.1245086037	C	5.9886979393	3.4874152943	-0.0512361297
C	5.1397782939	-2.1022359306	0.0577120015	H	5.3880301344	3.2227557846	-2.1103881788
H	5.6266261303	-2.7143496287	-1.9612306803	H	6.4157655469	4.1315574624	1.9694191674
H	4.5398769298	-1.9101577534	2.1259586154	C	6.5898517576	2.1304125764	0.0439259695
C	5.5135447517	-0.6658282015	-0.0572944774	C	6.3879369168	1.3805784985	1.2098406087
C	5.8770648556	0.1171101238	1.0497885147	C	7.1163657185	1.4539615387	-1.0665430571

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Table S1 – *Continued from previous page*

[8]CPP				**[10]CPP**			
C	5.1721098476	0.0199366434	-1.2307025609	C	6.5319330272	-0.0009019564	1.2121266891
C	5.6857316288	1.4948478428	1.0496261073	H	5.9853399461	1.8664260706	2.1015184594
H	6.2345655975	-0.3667244807	1.9627511112	C	7.2609436619	0.0707380730	-1.0641384552
C	4.9812039206	1.3957775218	-1.2309010861	H	7.3579138814	2.0115974947	-1.9752776608
H	4.8991475494	-0.5426512355	-2.1262312236	C	6.8846611475	-0.6966460825	0.0484463650
C	5.1228157480	2.1487263294	-0.0577660759	H	6.2373377245	-0.5563066670	2.1054280543
H	5.8973434262	2.0584120247	1.9622893829	H	7.6135140754	-0.4270548667	-1.9713536402
H	4.5658284397	1.8629997772	-2.1265551401	C	6.5742622022	-2.1481141737	-0.0442208319
				C	5.9723014329	-2.6388901534	-1.2101201028
				C	6.5996673246	-3.0020530315	1.0686131910
				C	5.2756797313	-3.8405370648	-1.2109440188
				H	5.9345932311	-2.0114662774	-2.1035281519
				C	5.9024920681	-4.2053416746	1.0676882250
				H	7.1215110709	-2.6920780985	1.9778467673
				C	5.1495179829	-4.6076372777	-0.0455038055
				H	4.7129992931	-4.1185911278	-2.1049731494
				H	5.8924818346	-4.8132883065	1.9761755723
				C	4.0481882844	-5.6025425818	0.0469687824
				C	3.2721268730	-5.6516540695	1.2123332532
				C	3.5710211181	-6.3090111075	-1.0671984538
				C	2.0052022139	-6.2210906275	1.2103843496
				H	3.6060996196	-5.1219169045	2.1074016432
				C	2.3024961255	-6.8787996353	-1.0692030550
				H	4.1770277973	-6.3592442424	-1.9756884425
				C	1.4552682351	-6.7673787441	0.0434894661
				H	1.3847969049	-6.1205718386	2.1038433615
				H	1.9406852808	-7.3643350648	-1.9794188335
				C	-0.0203707102	-6.9268655305	-0.0500014965

Table S2: Excited state (S_1) optimized geometries (given in Å) of [8] and [10]CPP at the TD-CAM-B3LYP/def-SV(P) level of theory.

	[8]CPP				**[10]CPP**		
C	0.2222661895	-5.4131678327	-1.2273005390	C	-7.1089850901	-0.5844051157	1.1335904663
C	1.5818314796	-5.1821866968	-1.2265866972	C	-6.8597941556	-1.9430838621	1.1357057320
C	2.3126232546	-5.0469826198	-0.0211664109	C	-6.4128377302	-2.6160036245	-0.0248279179
C	1.6261108570	-5.4476900635	1.1536277793	C	-6.4465269246	-1.8699416978	-1.2228408663
C	0.2674775421	-5.6789208281	1.1528028239	C	-6.6951633852	-0.5107397016	-1.2248458185
C	-0.5124882812	-5.5273368026	-0.0221608900	C	-6.9285922599	0.2011065080	-0.0283359821
H	-0.3009038870	-5.3722778351	-2.1837416662	H	-7.4033111296	-0.1075270621	2.0709849562
H	2.0632078391	-4.9704042290	-2.1824737031	H	-6.9661657137	-2.4906800450	2.0746588175
H	2.1597990299	-5.5057277784	2.1043679746	H	-6.1495035687	-2.3382816265	-2.1626643887
H	-0.2184646907	-5.9105143966	2.1027452207	H	-6.5825643343	0.0301355564	-2.1659349610
C	3.5465463773	-4.2713946507	0.0217793873	C	-5.7175641222	-3.9049841817	0.0292719977
C	4.2038103716	-3.8258280141	-1.1534916204	C	-5.1128870188	-4.3443446391	1.2268150622
C	3.9861887009	-3.6719477561	1.2270486398	C	-5.4002638997	-4.6457507187	-1.1325777177
C	5.0005605073	-2.7013353316	-1.1533948520	C	-4.1134402906	-5.2986634140	1.2268430870
H	4.0236527307	-4.3316676548	-2.1041197667	H	-5.3418815346	-3.8406500639	2.1674324668
C	4.7833922096	-2.5466035912	1.2271197133	C	-4.4013666015	-5.5996136988	-1.1325302830
H	3.5880955576	-4.0145549374	2.1833133134	H	-5.9170158590	-4.4320117471	-2.0706661227
C	5.2033112474	-1.9333352314	0.0217169861	C	-3.6466301100	-5.8824128890	0.0292883510
H	5.4181376149	-2.3638216227	-2.1041184908	H	-3.5997501443	-5.5040959221	2.1674943815
H	4.9744541759	-2.0578611241	2.1836202998	H	-4.1639546849	-6.1058314981	-2.0706821744
C	-1.9333352865	-5.2033122663	0.0217061023	C	-6.7326047292	1.6525008930	0.0253025567
C	-2.5466019718	-4.7834029758	1.2271129837	C	-6.6919864618	2.4569019457	-1.1370446525
C	-2.7013383736	-5.0005533268	-1.1534026641	C	-6.3249280598	2.2774033079	1.2236827783
C	-3.6719471094	-3.9862004905	1.2270502653	C	-6.0913766710	3.7005620243	-1.1355379719
H	-2.0578583900	-4.9744722994	2.1836114755	H	-7.0967344390	2.0746025880	-2.0766405563
C	-3.8258313430	-4.2038037712	-1.1534911329	C	-5.7234791711	3.5214996986	1.2250642915
H	-2.3638269933	-5.4181220392	-2.1041306840	H	-6.3656199968	1.7262521042	2.1646629926
C	-4.2713966082	-3.5465492371	0.0217855308	H	-6.0429618847	4.2568915710	-2.0741197304
H	-4.0145529096	-3.5881156011	2.1833186620	H	-5.3170946178	3.8938090027	2.1668807231
H	-4.3316735647	-4.0236396233	-2.1041169409	C	-2.3269749694	-6.5176161993	-0.0250430312
C	5.5273354473	-0.5124883080	-0.0221467130	C	-1.5803146588	-6.5171320062	-1.2231041431
C	5.6789136646	0.2674789497	1.1528169486	C	-1.6343898089	-6.9332594755	1.1355260550
C	5.4131724655	0.2222660219	-1.2272867160	C	-0.2112178136	-6.7040495128	-1.2251376187
C	5.4476840493	1.6261124950	1.1536392189	H	-2.0617321197	-6.2415393990	-2.1628336525
H	5.9105018650	-0.2184615617	2.1027612991	C	-0.2658340637	-7.1206970793	1.1333544013
C	5.1821926302	1.5818313162	-1.2265760023	H	-2.1767003263	-7.0644628346	2.0744012910

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Table S2 – *Continued from previous page*

[8]CPP				**[10]CPP**			
H	5.3722891925	-0.3009036848	-2.1837283838	C	0.5104558786	-6.9051945187	-0.0287458975
C	5.0469824671	2.3126245613	-0.0211575845	H	0.3240242787	-6.5675181623	-2.1662676011
H	5.5057174117	2.1598012359	2.1043791793	H	0.2241600418	-7.3935705656	2.0705071264
H	4.9704161039	2.0632060138	-2.1824651069	C	1.9516890764	-6.6445791227	0.0246575122
C	4.2713953246	3.5465480476	0.0217812864	C	2.5574781956	-6.2075272210	1.2224082884
C	3.8258261212	4.2038015179	-1.1534947032	C	2.7539128141	-6.5709604661	-1.1374949165
C	3.6719514977	3.9862029329	1.2270479226	C	3.7745233323	-5.5531237079	1.2230609656
C	2.7013338887	5.0005518538	-1.1534031017	H	2.0082279592	-6.2700026885	2.1632945664
H	4.3316631161	4.0236345132	-2.1041224909	C	3.9703734450	-5.9167379038	-1.1368301034
C	2.5466076940	4.7834068555	1.2271138949	H	2.3901325063	-6.9938932019	-2.0764632510
H	4.0145615911	3.5881206407	2.1833159702	C	4.4738841762	-5.2885214415	0.0256010205
C	1.9333359690	5.2033140582	0.0217085669	H	4.1284010720	-5.1292926935	2.1642742976
H	2.3638183878	5.4181192330	-2.1041302655	H	4.5242042783	-5.8461550405	-2.0754900164
H	2.0578682055	4.9744797569	2.1836139441	C	5.4871810021	-4.2310093303	-0.0276465302
C	0.5124892729	5.5273375417	-0.0221549769	C	5.7234559791	-3.5214915965	-1.2250617102
C	-0.2674768670	5.6789166581	1.1528094557	C	6.0913946477	-3.7005704171	1.1355304858
C	-0.2222669202	5.4131737170	-1.2272941563	C	6.3249070332	-2.2773941464	-1.2236821801
C	-1.6261100776	5.4476856911	1.1536337748	H	5.3170507830	-3.8937927267	-2.1668726689
H	0.2184646388	5.9105059988	2.1027530596	C	6.6920048790	-2.4569082728	1.1370353166
C	-1.5818318627	5.1821930210	-1.2265813560	H	6.0429909164	-4.2569042449	2.0741104206
H	0.3009008229	5.3722912489	-2.1837368139	C	6.7326065190	-1.6525038569	-0.0253067394
C	-2.3126233348	5.0469826193	-0.0211617020	H	6.3655787302	-1.7262332236	-2.1646577987
H	-2.1597978072	5.5057192459	2.1043743801	H	7.0967657206	-2.0746121058	2.0766273750
H	-2.0632077713	4.9704161930	-2.1824696770	C	6.9285951929	-0.2011043637	0.0283351079
C	-3.5465458280	4.2713945852	0.0217805490	C	6.6951501694	0.5107371493	1.2248415037
C	-4.2038023920	3.8258232509	-1.1534930476	C	7.1089978536	0.5844071335	-1.1335865313
C	-3.9861963919	3.6719519271	1.2270492082	C	6.4465136575	1.8699407258	1.2228367128
C	-5.0005521843	2.7013306942	-1.1533973097	H	6.5825384022	-0.0301404512	2.1659278259
H	-4.0236391100	4.3316589885	-2.1041220638	C	6.8598062767	1.9430875131	-1.1357027055
C	-4.7833995427	2.5466075480	1.2271191346	H	7.4033287557	0.1075304179	-2.0709802526
H	-3.5881112477	4.0145639579	2.1833154945	C	6.4128407114	2.6160039348	0.0248264738
C	-5.2033103131	1.9333343545	0.0217158545	H	6.1494760427	2.3382783376	2.1626568737
H	-5.4181225821	2.3638139705	-2.1041226279	H	6.9661845060	2.4906846641	-2.0746544996
H	-4.9744691982	2.0578695689	2.1836204678	C	5.7175655064	3.9049874809	-0.0292767076
C	-5.5273346764	0.5124876193	-0.0221458948	C	5.1128812226	4.3443377909	-1.2268179863
C	-5.6789125682	-0.2674782457	1.1528186931	C	5.4002719512	4.6457590762	1.1325696579
C	-5.4131726761	-0.2222685363	-1.2272849955	C	4.1134337089	5.2986568297	-1.2268466584
C	-5.4476847245	-1.6261121361	1.1536425635	H	5.3418695770	3.8406354541	-2.1674328274

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Table S2 – *Continued from previous page*

[8]CPP				**[10]CPP**			
H	-5.9104988968	0.2184638286	2.1027625976	C	4.4013733217	5.5996218488	1.1325224950
C	-5.1821944168	-1.5818338554	-1.2265723538	H	5.9170284254	4.4320241471	2.0706566620
H	-5.3722903181	0.3008992815	-2.1837275191	C	3.6466309311	5.8824134380	-0.0292933564
C	-5.0469849564	-2.3126260981	-0.0211533767	H	3.5997368878	5.5040819899	-2.1674959552
H	-5.5057170852	-2.1597986625	2.1043835471	H	4.1639654677	6.1058442448	2.0706729293
H	-4.9704200560	-2.0632107617	-2.1824605563	C	2.3269750433	6.5176164600	0.0250406624
				C	1.5803178311	6.5171329580	1.2231036869
				C	1.6343866054	6.9332574604	-1.1355272178
				C	0.2112212879	6.7040496293	1.2251409451
				H	2.0617383378	6.2415423603	2.1628322377
				C	0.2658310882	7.1206940123	-1.1333525584
				H	2.1766949308	7.0644602087	-2.0744038531
				C	-0.5104569325	6.9051914244	0.0287502484
				H	-0.3240171808	6.5675201969	2.1662730678
				H	-0.2241647209	7.3935667876	-2.0705044239
				C	-1.9516877278	6.6445772502	-0.0246493326
				C	-2.5574875797	6.2075435227	-1.2224033542
				C	-2.7539055453	6.5709424686	1.1375079618
				C	-3.7745314478	5.5531410416	-1.2230572170
				H	-2.0082464114	6.2700359516	-2.1632935211
				C	-3.9703649664	5.9167211402	1.1368424340
				H	-2.3901202902	6.9938639529	2.0764791861
				C	-4.4738845912	5.2885177697	-0.0255947266
				H	-4.1284171895	5.1293291642	-2.1642757925
				H	-4.5241895696	5.8461277391	2.0755046720
				C	-5.4871785112	4.2310099704	0.0276462735

Table S3: Excited state (S_2) optimized geometries (given in Å) of [8] and [10]CPP at the TD-CAM-B3LYP/def-SV(P) level of theory.

	[8]CPP				**[10]CPP**		
C	-4.4423581877	2.9495559483	-1.1995231115	C	-7.1759189845	0.4243508281	-1.0977595517
C	-5.1380730528	1.7556710643	-1.2506298955	C	-6.8743679045	1.7759070269	-1.1206270074
C	-5.5761569985	1.1062004899	-0.0703537120	C	-6.3565060289	2.4309747459	0.0122373057
C	-5.5198393998	1.8830874498	1.1161669285	C	-6.3424584651	1.6983474549	1.2113325080
C	-4.8277944260	3.0786510113	1.1602171964	C	-6.6444807613	0.3472826544	1.2383184704
C	-4.1555436252	3.5819272855	0.0261320441	C	-6.9710506039	-0.3587670004	0.0609680202
H	-3.9944050236	3.3264183671	-2.1213585368	H	-7.5289114420	-0.0471740176	-2.0174414785
H	-5.2134212862	1.2468118653	-2.2127976662	H	-6.9947522451	2.3268453043	-2.0569038623
H	-5.9619232528	1.5020718205	2.0392752804	H	-5.9701969621	2.1658068322	2.1255092299
H	-4.7435517333	3.6016589451	2.1162523054	H	-6.4986088685	-0.1936309006	2.1747454816
C	-5.7457246747	-0.3420345844	-0.0485797954	C	-5.6170704432	3.7110813708	-0.0750695067
C	-5.7520176041	-1.1208572363	-1.2393867984	C	-4.8862402733	4.0075690863	-1.2356527853
C	-5.5781084912	-1.0720187939	1.1584767487	C	-5.4052711647	4.5429413062	1.0374485603
C	-5.3062678234	-2.4235186538	-1.2448410124	C	-3.8810853599	4.9649713339	-1.2319455453
H	-6.0427126791	-0.6639033763	-2.1878588759	H	-5.0188003266	3.3946644373	-2.1298207865
C	-5.1309068017	-2.3759647853	1.1514503457	C	-4.3993111048	5.5011173503	1.0406713791
H	-5.6664279837	-0.5627504495	2.1195881158	H	-6.0045161947	4.4032613794	1.9407602959
C	-4.8241900533	-3.0453407662	-0.0613867590	C	-3.5555727871	5.6764273110	-0.0681319164
H	-5.2581305454	-2.9562234828	-2.1973301366	H	-3.2584665511	5.0719058327	-2.1230285656
H	-4.8837573263	-2.8403222826	2.1076550757	H	-4.2318184000	6.0895385106	1.9465138238
C	-2.9856678253	4.4803394917	0.1331143975	C	-6.8389307217	-1.8177528601	0.0141080875
C	-2.1997219596	4.4434491883	1.2971123374	C	-6.7621600799	-2.6091704819	1.1872106475
C	-2.4369291483	5.1577211707	-0.9717920369	C	-6.5205405039	-2.4759188403	-1.1973439293
C	-0.8761263007	4.8589747907	1.2900485778	C	-6.1838397662	-3.8602317004	1.1772089486
H	-2.5798909371	3.9496333162	2.1935681790	H	-7.1193276884	-2.2065135449	2.1375932180
C	-1.1118217322	5.5744636432	-0.9779204759	C	-5.9420618999	-3.7282423868	-1.2100093864
H	-3.0361544919	5.3001958479	-1.8747305922	H	-6.6164542373	-1.9442607442	-2.1456029793
C	-0.2656907035	5.3372305727	0.1200050702	H	-6.1044038799	-4.4044531796	2.1204439325
H	-0.2716632276	4.6741591287	2.1804921268	H	-5.6103172648	-4.1304573138	-2.1683036409
H	-0.7082563928	6.0303039003	-1.8857820262	C	-2.2398622379	6.3544096238	0.0264606370
C	-3.8115532257	-4.0998195497	-0.0949331425	C	-1.4993747207	6.2639523643	1.2152283577
C	-3.3239348369	-4.7244700651	1.0789470766	C	-1.5759412606	6.8813765488	-1.0946461047
C	-3.0551706897	-4.3189547923	-1.2690075457	C	-0.1363637518	6.5146772670	1.2394992964
C	-2.0612234071	-5.2896140087	1.1236991381	H	-1.9736077920	5.8731629014	2.1182576452
H	-3.9168019565	-4.6998890632	1.9959218547	C	-0.2121370665	7.1321080844	-1.0733794994
C	-1.7910418095	-4.8806539706	-1.2178883131	H	-2.1298638386	7.0501251612	-2.0217842793

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Table S3 – *Continued from previous page*

	[8]CPP				**[10]CPP**		
H	-3.3969115432	-3.9119986026	-2.2219261809	C	0.5677233348	6.8637572961	0.0709177796
C	-1.2100713093	-5.2733220331	0.0011001776	H	0.4093255439	6.3109067292	2.1625272655
H	-1.6975012606	-5.6889124295	2.0740223937	H	0.2674625263	7.4960165344	-1.9848828006
H	-1.1908987863	-4.8870477285	-2.1303031050	C	2.0275016963	6.6934175368	0.0137645938
C	0.2657143603	-5.3372287027	0.1199841258	C	2.6606299772	6.3402202663	-1.1979576857
C	1.1116012003	-5.5744521115	-0.9781318433	C	2.8265538304	6.6177905870	1.1782670772
C	0.8764122637	-4.8589839871	1.2898955131	C	3.9058175537	5.7439828616	-1.2174017480
C	2.4367081678	-5.1577045512	-0.9723003222	H	2.1143831114	6.4232292878	-2.1393886993
H	0.7078326512	-6.0302862248	-1.8859055132	C	4.0704747070	6.0209866601	1.1630430250
C	2.2000097032	-4.4434574351	1.2966646084	H	2.4369054094	6.9912263982	2.1280938778
H	0.2721524318	-4.6741802215	2.1804790875	C	4.6055295306	5.4485538950	-0.0206434553
C	2.9856932062	-4.4803317444	0.1324890397	H	4.2885477247	5.3869993846	-2.1745550971
H	3.0357303521	-5.3001706905	-1.8753749221	H	4.6223993985	5.9446736772	2.1020252097
H	2.5803827226	-3.9496507929	2.1930391379	C	5.6326447169	4.4153632831	0.0083247245
C	4.1555428119	-3.5819167583	0.0252534186	C	5.9421699837	3.7282883240	1.2099515754
C	4.8280477495	-3.0786503815	1.1591929622	C	6.1837741030	3.8602099217	-1.1772836462
C	4.4420886671	-2.9495366901	-1.2004606375	C	6.5206461855	2.4759628782	1.1972798180
C	5.5200909596	-1.8830919096	1.1149980190	H	5.6105155883	4.1305360438	2.1682630717
H	4.7440146228	-3.6016649462	2.1152428100	C	6.7620911239	2.6091470590	-1.1872920097
C	5.1378020612	-1.7556578721	-1.2517141664	H	6.1042687475	4.4043974042	-2.1205319309
H	3.9939320086	-3.3263898041	-2.1222009865	C	6.8389414857	1.8177587187	-0.0141758788
C	5.5761522245	-1.1061972030	-0.0715307737	H	6.6166394496	1.9443398741	2.1455503485
H	5.9623834526	-1.5020855001	2.0380102849	H	7.1191882374	2.2064670325	-2.1376909417
H	5.2129414812	-1.2467898735	-2.2138938539	C	6.9710487217	0.3587690804	-0.0610134775
C	5.7457273500	0.3420362497	-0.0497887219	C	6.6444832365	-0.3473012102	-1.2383525700
C	5.7517901905	1.1208612547	-1.2405965284	C	7.1759063728	-0.4243318237	1.0977267104
C	5.5783373318	1.0720174287	1.1573019190	C	6.3424566460	-1.6983649005	-1.2113459599
C	5.3060311820	2.4235193292	-1.2459623650	H	6.4986240587	0.1935913889	-2.1747930017
H	6.0423114343	0.6639100861	-2.1891234395	C	6.8743507709	-1.7758869874	1.1206159570
C	5.1311249560	2.3759599231	1.1503637599	H	7.5288890275	0.0472037149	2.0174064305
H	5.6668381072	0.5627445558	2.1183942360	C	6.3564959535	-2.4309731617	-0.0122396471
C	4.8241750652	3.0453359000	-0.0624143473	H	5.9702006830	-2.1658382003	-2.1255177701
H	5.2577124983	2.9562295761	-2.1984394366	H	6.9947264366	-2.3268076448	2.0569041139
H	4.8841473130	2.8403125406	2.1066154680	C	5.6170588491	-3.7110784861	0.0750842526
C	3.8115277371	4.0998096529	-0.0957643617	C	4.8862264333	-4.0075496244	1.2356700326
C	3.3241657266	4.7244958643	1.0782033186	C	5.4052628392	-4.5429552525	-1.0374215789
C	3.0548874947	4.3189041847	-1.2696797367	C	3.8810732868	-4.9649536863	1.2319754654
C	2.0614649424	5.2896441849	1.1232114218	H	5.0187834329	-3.3946312484	2.1298290326

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Table S3 – *Continued from previous page*

	[8]CPP				**[10]CPP**		
H	3.9172329542	4.6999453509	1.9950494015	C	4.3993044334	-5.5011331028	-1.0406320854
C	1.7907701073	4.8806059198	-1.2183035460	H	6.0045098367	-4.4032888831	-1.9407341506
H	3.3964185303	3.9119110332	-2.2226577557	C	3.5555639752	-5.6764286228	0.0681721906
C	1.2100686838	5.2733180056	0.0007987784	H	3.2584539124	-5.0718753064	2.1230594818
H	1.6979502922	5.6889744342	2.0736005959	H	4.2318161052	-6.0895686732	-1.9464659160
H	1.1904269023	4.8869678177	-2.1305865492	C	2.2398578156	-6.3544191105	-0.0264108921
				C	1.4993789372	-6.2640077161	-1.2151883492
				C	1.5759290707	-6.8813508372	1.0947087894
				C	0.1363689096	-6.5147355653	-1.2394609939
				H	1.9736178599	-5.8732508625	-2.1182286102
				C	0.2121263316	-7.1320851223	1.0734411451
				H	2.1298452524	-7.0500702518	2.0218560118
				C	-0.5677275425	-6.8637721974	-0.0708708809
				H	-0.4093138501	-6.3110002641	-2.1625006704
				H	-0.2674786695	-7.4959660464	1.9849525084
				C	-2.0275025845	-6.6934240186	-0.0137296155
				C	-2.6606301417	-6.3401742200	1.1979794105
				C	-2.8265534360	-6.6178388876	-1.1782376843
				C	-3.9058127400	-5.7439282367	1.2173987221
				H	-2.1143822949	-6.4231459705	2.1394129183
				C	-4.0704704490	-6.0210283936	-1.1630383689
				H	-2.4369062171	-6.9913190170	-2.1280475447
				C	-4.6055222352	-5.4485458933	0.0206267217
				H	-4.2885394422	-5.3868927252	2.1745341723
				H	-4.6224023228	-5.9447553869	-2.1020198225
				C	-5.6326286361	-4.4153522001	-0.0083780732

Convergence of the MD snapshot sampling geometries

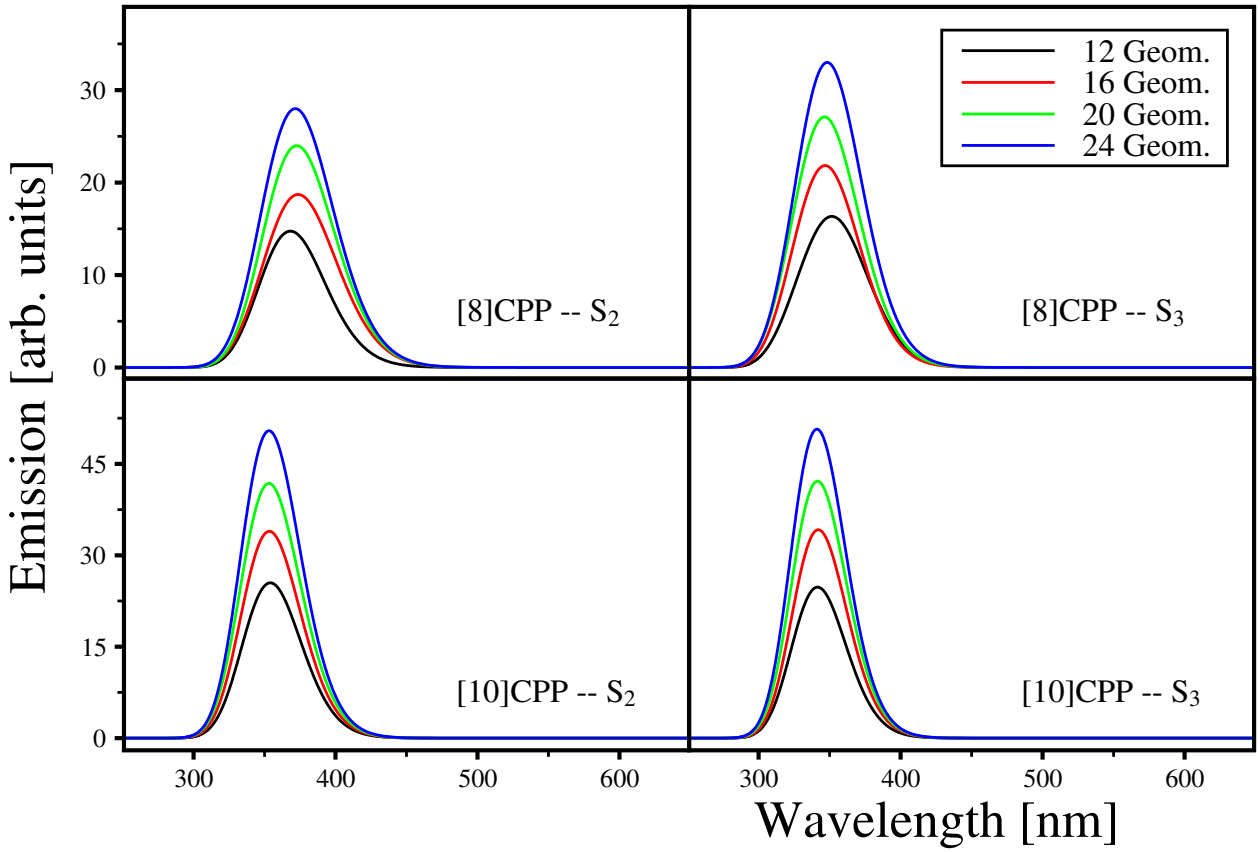

Figure S5: Simulated S_2 and S_3 emission bands for different number of MD snapshot sampling geometries.

Table S4: Randomly selected S_2 MD snapshot geometries used for computing the fluorescence spectrum of [8]CPP at the TD-CAM-B3LYP/def-SV(P)←TD-DFTB/MD level of theory.

(12 Geometries)		(16 Geometries)		(20 Geometries)		(24 Geometries)	
Trajectory	Snapshot	Trajectory	Snapshot	Trajectory	Snapshot	Trajectory	Snapshot
01	2530	01	7540	01	2530	01	2530
01	7540	01	9770	01	7540	01	7540
02	3440	02	3440	01	9770	01	9770
02	5620	02	5620	02	3440	02	3440
02	7160	03	3260	02	5620	02	5620
03	3260	03	7670	02	7160	02	7160
04	0740	04	9550	03	3260	03	3260
05	8570	05	4210	03	7670	03	7670
06	5030	06	5030	04	0740	04	0740
06	8910	07	3470	04	9550	04	9550
07	2370	07	6480	05	4210	05	4210
09	5340	08	5380	05	8570	05	8570
		08	9960	06	5030	06	5030
		09	5340	06	8910	06	8910
		09	6350	07	2370	07	2370
		10	1640	07	3470	07	3470
				07	6480	07	6480
				09	5340	08	1020
				09	6350	08	5380
				10	1640	08	9960
						09	5340
						09	6350
						10	1640
						10	3890

Table S5: Randomly selected S_3 MD snapshot geometries used for computing the fluorescence spectrum of [8]CPP at the TD-CAM-B3LYP/def-SV(P)←TD-DFTB/MD level of theory.

(12 Geometries)		(16 Geometries)		(20 Geometries)		(24 Geometries)	
Trajectory	Snapshot	Trajectory	Snapshot	Trajectory	Snapshot	Trajectory	Snapshot
01	0330	01	1240	01	1240	01	0330
01	3960	01	3960	01	3840	01	1240
01	9090	02	2230	01	9090	01	3840
02	2230	02	3300	02	2230	01	3960
02	4060	02	4060	02	3300	01	9090
02	4290	02	4290	02	4060	02	2230
02	6810	02	8820	02	4290	02	3300
02	8820	03	0950	02	6810	02	4060
03	7190	03	4290	02	8820	02	4290
03	7960	03	7110	03	0820	02	6810
04	0740	03	7190	03	0950	02	8820
04	8780	03	7960	03	4290	03	0820
		03	9400	03	7040	03	0950
		04	0740	03	7110	03	4290
		04	7490	03	7190	03	7040
		04	8780	03	7960	03	7110
				03	9400	03	7190
				04	0740	03	7960
				04	6790	03	9400
				04	7490	04	0740
						04	2330
						04	6790
						04	7490
						04	8780

Table S6: Randomly selected S_2 MD snapshot geometries used for computing the fluorescence spectrum of [10]CPP at the TD-CAM-B3LYP/def-SV(P)←TD-DFTB/MD level of theory.

(12 Geometries)		(16 Geometries)		(20 Geometries)		(24 Geometries)	
Trajectory	Snapshot	Trajectory	Snapshot	Trajectory	Snapshot	Trajectory	Snapshot
01	7540	01	1150	01	1150	01	1150
02	6860	01	7540	01	7540	01	7540
03	2610	02	6860	03	2610	02	6860
03	7250	03	4520	03	4520	03	2610
04	9460	03	7250	04	2910	03	4520
05	1370	04	1060	04	8010	03	7250
05	4380	04	2910	04	9460	04	1060
06	6590	04	8010	05	1370	04	2910
07	3190	05	1370	05	4380	04	8010
08	2200	05	4380	06	0970	04	9460
10	3160	06	6590	06	3900	05	1370
10	5590	07	3190	06	5700	05	4380
		08	5820	06	6590	06	0970
		09	2980	08	2200	06	3900
		10	4110	08	5820	06	5700
		10	5590	08	9700	06	6590
				09	2980	07	3190
				10	3160	08	2200
				10	4110	08	5820
				10	5590	08	9700
						09	2980
						10	3160
						10	4110
						10	5590

Table S7: Randomly selected S_3 MD snapshot geometries used for computing the fluorescence spectrum of [10]CPP at the TD-CAM-B3LYP/def-SV(P)←TD-DFTB/MD level of theory.

(12 Geometries)		(16 Geometries)		(20 Geometries)		(24 Geometries)	
Trajectory	Snapshot	Trajectory	Snapshot	Trajectory	Snapshot	Trajectory	Snapshot
01	6690	01	3310	01	0890	01	0890
02	1070	01	6690	01	3310	01	2170
02	4710	02	0880	01	6690	01	3310
02	4850	02	1010	02	0880	01	6690
02	8420	02	1070	02	1010	02	0880
03	3300	02	2920	02	1070	02	1010
03	3670	02	4710	02	2920	02	1070
03	4820	02	4850	02	4710	02	2920
03	6140	02	8420	02	4850	02	4710
04	2080	03	3300	02	8420	02	4850
04	4450	03	3670	03	3300	02	8420
04	7490	03	4820	03	3670	03	3300
		03	5830	03	6140	03	3670
		03	6140	03	7350	03	4820
		03	7350	03	7660	03	5830
		04	9320	04	1390	03	6140
				04	2080	03	7350
				04	4450	03	7660
				04	5730	04	1390
				04	9320	04	2080
						04	4450
						04	5730
						04	7490
						04	9320

References

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