Supporting Information for

Theoretical Rationalization of the Dual Photophysical Behavior of C_{60}^+

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Table S1. Optimized UB3LYP/6-31G* Cartesian coordinates (in Å) for the D_{5d} D₀ minimum.

С	0.71862261	3.40307143	0.59903337
С	-0.71862261	3.40307143	0.59903337
С	-1.41889730	3.17553839	-0.59903337
С	-0.69521163	2.95302011	-1.84543518
С	0.69521163	2.95302011	-1.84543518
С	1.41889730	3.17553839	-0.59903337
С	1.17330364	2.79767860	1.84543518
С	0.00000000	2,42257301	2.61473350
C	-1.17330364	2.79767860	1.84543518
Ċ	-2.29817969	1,98040830	1.84543518
Č	-2.58165311	2.33074685	-0.59903337
Č	-1 42395269	1 95990274	-2.61473350
Č	-0 72686134	1 00043881	-3 34938832
Č	0 72686134	1 00043881	-3 34938832
C	1 42395269	1 95990274	-2 61473350
C	2 59365681	1 57371895	-1 84543518
C C	2.59505001	2 33074685	-0 59903337
C	3 01444666	1 73505762	0 59903337
C	2 2981 7969	1 98040830	1 84543518
C C	0.00000000	1 23661037	3 3/038832
C	1 17608635	0.38213362	3.34938832
C	2 20400285	0.38213302	2 61 472 250
C	2.30400383	0.74601023	2.014/3330
C	3.02332122	-0.23134/64	1.64343316
C	2 45957096	0.30813019	0.59905557
C	3.4383/980	-0.30813019	-0.39903337
C	3.02332122	0.23134/84	-1.84343318
C	2.30400383	-0.74801023	-2.014/3330
C	1.1/608635	-0.38213362	-3.34938832
C	-2.59305081	1.5/3/1895	-1.84543518
C	-1.1/330364	-2./9/6/860	-1.84543518
C	-2.2981/969	-1.98040830	-1.84543518
C	-3.01444666	-1./3505/62	-0.59903337
C	-2.58165311	-2.330/4685	0.59903337
C	-1.41889/30	-3.1/553839	0.59903337
C	0.71862261	-3.4030/143	-0.59903337
C	1.17330364	-2.79767860	-1.84543518
C	-0.00000000	-2.42257301	-2.61473350
C	-0.00000000	-1.23661037	-3.34938832
C	-1.17608635	-0.38213362	-3.34938832
C	-2.30400385	-0.74861623	-2.61473350
C	-3.45857986	-0.36815619	-0.59903337
С	-3.45857986	0.36815619	0.59903337
С	-3.02332122	-0.25134784	1.84543518
С	-2.59365681	-1.57371895	1.84543518
С	-1.42395269	-1.95990274	2.61473350
С	-0.69521163	-2.95302011	1.84543518
С	0.69521163	-2.95302011	1.84543518
С	1.41889730	-3.17553839	0.59903337
С	2.29817969	-1.98040830	-1.84543518
С	3.01444666	-1.73505762	-0.59903337
С	2.58165311	-2.33074685	0.59903337
С	2.59365681	-1.57371895	1.84543518
С	1.42395269	-1.95990274	2.61473350
С	0.72686134	-1.00043881	3.34938832
С	-0.72686134	-1.00043881	3.34938832
С	-1.17608635	0.38213362	3.34938832
С	-2.30400385	0.74861623	2.61473350
С	-3.02332122	0.25134784	-1.84543518
С	-3.01444666	1.73505762	0.59903337
С	-0.71862261	-3.40307143	-0.59903337

 $E(D_0) = -2285.9118260 a.u.$

Table S2. Optimized UB3LYP/6-31G* Cartesian coordinates (in Å) for the C_i D₅ minimum.

~	0 (01001015411	0.546000044001	0 0 (0 0 0 1 1 5 4 5 4 0
C	0.691201915411	2.546900044301	2.360331154548
С	0.747088621830	1.350768256949	3.193870157398
С	-0.418365791743	0.642786522391	3.461938864715
Ċ	-1 694063081178	1 092116455425	2 919111583025
c	1,755000007000	2 2222 40222210	2.010111000020
C	-1./5580098/908	2.233348322218	2.12/166284583
С	-0.536889701316	2.979585365708	1.836560469725
С	1.884948340477	2.575880503416	1.548608501945
С	2 684395780044	1 405921474735	1 862617037987
č	1 080606311647	0.645549201705	2 881772323250
c	1.0072(5524042	0.045549201705	2.001772525255
C	1.99/365534843	-0./4/4082042/6	2.84484/538912
С	-0.404488466159	-0.814678777060	3.425257661124
С	-2.463421164158	-0.088060280483	2.549410361167
С	-3.260553398276	-0.072186710834	1.401022187477
С	-3 323668273167	1 126170817513	0 578035827537
Ĉ	-2 587898926119	2 255315437315	0.934940704698
c	1 997500225262	2.233313437313	0.095401740952
C	-1.88/300233262	3.010382233070	-0.083401749832
С	-0.625264247099	3.462359779099	0.477587175459
С	0.525314299192	3.494384098240	-0.322662351575
С	1.812426140310	3.039259298045	0.225507068232
С	3 375490198043	0 741901204650	0 847710702420
č	3 296739191828	1 223931952367	-0 520128721621
c	2 522020 400070	2 255272(12412	-0.520120721021
C	2.533039400979	2.3553/3613413	-0.819961111902
С	1.693469748437	2.3/15414014/4	-2.010/249/14/5
С	0.457180266952	3.086757141020	-1.701708520394
С	-0.754787112941	2.650791188325	-2.245470635367
С	-1.950626667055	2.617184414671	-1.421184782994
Ĉ	-2 719312995838	1 440816008694	-1 792030345237
c	2 2022 40202 204	0.711120501860	0.812260241144
C	-3.393340393304	0.711120391809	-0.812209241144
C	-1.6622884/1/24	-1.251106327508	2.8636/24/5/5/
С	-1.884948340477	-2.575880503416	-1.548608501945
С	-1.812426140310	-3.039259298045	-0.225507068232
С	-0.525314299192	-3.494384098240	0.322662351575
С	0 625264247099	-3 462359779099	-0 477587175459
č	0.536889701316	2 070585365708	1 836560460725
c	0.330003701310	1 250769256040	2 102070157200
C	-0./4/088021830	-1.330/08230949	-3.1938/013/398
C	-1.98069631164/	-0.645549201/05	-2.881//2323259
С	-2.684395780044	-1.405921474735	-1.862617037987
С	-3.375490198043	-0.741901204650	-0.847710702420
С	-3.296739191828	-1.223931952367	0.520128721621
С	-2 533039400979	-2 355373613413	0 819961111902
č	0.457180266952	3 086757141020	1 701708520304
C	-0.45/180200952	-5.000757141020	2.245470(252(7
C	0./34/8/112941	-2.030/91188323	2.2434/063336/
C	1.950626667055	-2.61/1844146/1	1.421184/82994
С	1.887500235262	-3.016582235670	0.085401749852
С	2.587898926119	-2.255315437315	-0.934940704698
С	1.755800987908	-2.233348322218	-2.127166284583
С	1 694063081178	-1 092116455425	-2 919111583025
c	0.418265701742	0.642786522201	2.010111000020
C	0.410303791743	-0.042/80322391	-3.401930004713
C	-1.99/365534843	0./4/4082042/6	-2.84484/538912
С	-0.779474995439	1.495824362432	-3.1204/0/8/454
С	0.404488466159	0.814678777060	-3.425257661124
С	1.662288471724	1.251106327508	-2.863672475757
С	2.463421164158	0.088060280483	-2.549410361167
č	3 260553398276	0.072186710834	-1 401022187477
č	2 272660333370270	1 1 261 7001 7512	0 578025077577
C	3.3230082/310/	-1.1201/081/313	-0.3/803382/33/
C	3.393340393304	-0.711120591869	0.812269241144
С	2.719312995838	-1.440816008694	1.792030345237
С	-1.693469748437	-2.371541401474	2.010724971475
С	0.779474995439	-1.495824362432	3.120470787454
C	-0.691201915411	-2.546900044301	-2.360331154548
-			

 $E(D_5) = -2285.8630290 a.u.$

Table S3. Optimized UB3LYP/6-31G* Cartesian coordinates (in Å) for the $C_i D_5/D_4$ MECI.

С	0.5770056452	0.7625127394	-3.3151314771
С	0.5116593875	-0.7039692433	-3.3327840395
С	1.5462289132	-1.4245097473	-2.7808827236
С	2.7127147516	-0.7848376530	-2.2050496873
С	2.7773213211	0.6198470675	-2.1752813673
С	1.6835786104	1.4027160768	-2.7425415416
С	-0.7653777756	1.2511089464	-3.1353185743
С	-1.6766914974	0.1415986510	-3.0157508791
С	-0.8887789105	-1.0887608256	-3.1462364639
С	-1.2485549588	-2.1937971515	-2.4088091043
С	1.2314392663	-2.6227672556	-1.9574658341
С	3.1268878676	-1.5642053668	-1.0666382760
С	3.5322230838	-0.9179508489	0.0630809305
С	3.6092348745	0.5813441221	0.0915723878
С	3.2619307457	1.3091187357	-1.0115445876
С	2.4511003246	2.5642405027	-0.8631904329
С	1.4933904998	2.5888855527	-1.9381353591
С	0.1753973145	3.1051602238	-1.7581421554
С	-0.9750619684	2.3964623823	-2.3468150541
С	-2.7757399598	0.1757754291	-2.1477303481
С	-3.0154740562	1.3479189490	-1.3361221683
С	-2.1398924062	2.4672796005	-1.4495803032
С	-1.7255496606	3.1505300831	-0.3031059713
С	-0.2311764159	3.5619361213	-0.5032416342
С	0.6687664280	3.5190347400	0.5726000840
С	2.0668998930	2.9923405769	0.3724112991
С	2.3967200323	2.1910827686	1.5229196692
С	3.1493581892	1.0106977854	1.3834383505
С	2.1864732303	-2.7363208722	-0.9540926428
С	0.7653777756	-1.2511089464	3.1353185743
С	0.9750619684	-2.3964623823	2.3468150541
С	-0.1753973145	-3.1051602238	1.7581421554
С	-1.4933904998	-2.5888855527	1.9381353591
С	-1.6835786104	-1.4027160768	2.7425415416
С	-0.5116593875	0.7039692433	3.3327840395
С	0.8887789105	1.0887608256	3.1462364639
С	1.6766914974	-0.1415986510	3.0157508791
С	2.7757399598	-0.1757754291	2.1477303481
С	3.0154740562	-1.3479189490	1.3361221683
С	2.1398924062	-2.4672796005	1.4495803032
С	0.2311764159	-3.5619361213	0.5032416342
С	-0.6687664280	-3.5190347400	-0.5726000840
С	-2.0668998930	-2.9923405769	-0.3724112991
С	-2.4511003246	-2.5642405027	0.8631904329
С	-3.2619307457	-1.3091187357	1.0115445876
С	-2.7773213211	-0.6198470675	2.1752813673
С	-2.7127147516	0.7848376530	2.2050496873
С	-1.5462289132	1.4245097473	2.7808827236
С	1.2485549588	2.1937971515	2.4088091043
С	0.1816285167	3.0114111905	1.7690128593
С	-1.2314392663	2.6227672556	1.9574658341
С	-2.1864732303	2.7363208722	0.9540926428
С	-3.1268878676	1.5642053668	1.0666382760
С	-3.5322230838	0.9179508489	-0.0630809305
С	-3.6092348745	-0.5813441221	-0.0915723878
С	-3.1493581892	-1.0106977854	-1.3834383505
С	-2.3967200323	-2.1910827686	-1.5229196692
С	1.7255496606	-3.1505300831	0.3031059713
С	-0.1816285167	-3.0114111905	-1.7690128593
С	-0.5770056452	-0.7625127394	3.3151314771

 $E(D_4) = -2285.8064886 a.u.$

 $E(D_5) = -2285.8063178 a.u.$

Figure S1. Absorption spectra simulated using the first nine excited states computed at TD-DFT/SV level within the NE approach for an ensemble of (a) 240, (b) 310, (c) 341 and (d) 372 geometries. The error due to the statistical sampling is shown as a shaded blue area.



Figure S2. Absorption spectra simulated using the first fifteen excited states computed at TD-DFT/6-31G* level within the NE approach for an ensemble of 240 geometries (see Figure 2). The error due to the statistical sampling is shown as a shaded blue area.



Figure S3. D_4 and D_5 energy gradients at the $C_i D_5/D_4$ MECI.



D₄ energy gradient



D₅ energy gradient