Electronic Supplementary Material (ESI) for RSC Advances.

Electronic Supplementary Information

Photophysics of Chlorin e6:

From One- and Two- Photon Absorption to Fluorescence and Phosphorescence

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Content

1. Details on the Wigner Distribution

The phase space around the S_0, S_1 and T_1 minima structures was sampled via a Wigner distribution.[S1,S2] As input, a set of vibrational frequencies and the corresponding normal mode vectors were provided by a frequency calculation performed at the B3LYP/6-31G* level of theory for S_0 and T_1, and at the CAM-B3LYP/6-31+G* level of theory for S_1.

[S1] J. P. Dahl, M. Springborg *J. Chem. Phys.* **1988**, *88*, 4535-4547.
[S2] R. Schinke *Photodissociation Dynamics: Spectroscopy and Fragmentation of Small Polyatomic Molecules* (Cambridge University Press), 1995.

2. Benchmark of the Static Absorption Spectrum

After optimization on the ground state (S_0) at the B3LYP/6-31G* level of theory, different DFT functionals and basis sets were tested (Table S1). In all calculations the solvent (water) effect was included via the PCM. The CAM-B3LYP/6-31+G* level of theory was finally selected for its capability to agree with the experimental absorption maximum, 1.92 eV (644 nm), being at the same time computationally affordable.

Table S1. $S_0 \rightarrow S_1$ absorption values for chlorin e6 given in eV and, in parentheses, in nm (PCM: water).

Basis set	Functional		
	B3LYP	CAM-B3LYP	M06-2X
6-31+G*	2.076 (597)	1.985 (625)	2.052 (604)
6-311+G*	2.068 (599)	1.974 (628)	2.040 (608)
6-311+G**	2.066 (600)	1.972 (629)	2.038 (609)

3. Analysis of the vibrational frequencies for S_0, S_1 and T_1 minima structures

Vibrational frequencies were computed for all fully optimized structures: ground state S_0 and T_1 minima at the B3LYP/6-31G* level of theory; excited state S_1 minimum at the CAM-B3LYP/6-31+G* level of theory.

All computed frequencies correspond to positive values. More in detail, the lowest-frequency high-amplitude modes were analyzed, in order to monitor the corresponding molecular vibrations. As shown in Table S2, they all correspond to out-of-plane bending vibrations, that couple several normal modes within the chlorin ring.

Table S2. Low-frequency values (given in cm^{-1}) of S_0, S_1 and T_1 minima structures.

Vibration	ν_{S0}	ν_{S1}	ν_{T1}
Out-of-plane twisting	14.97	16.55	15.57
Out-of-plane wagging	20.80	22.16	21.01
	24.79		
	32.89	32.90	31.12

4. Force Field and Related Molecular Dynamics Details

To achieve a better description of the dynamic behavior of Ce6, and thus a better modeling of its electronic structure, the dihedral parameters along the conjugated carbon cycle were strengthened; hence the rigidity of the conjugated macrocycle was ensured. Indeed, the original gaff parameters are fitted to reproduce small molecular residues and not large highly delocalized ones.

A new atom type (cz) has been created to define the C2 atom (see the atom numbering scheme in Figure S1), and particularly in order to obtain a better description of its structural vicinity. Although, standard gaff parameters have been used for all the bonds, angles and dihedrals involving this atom, the definition of a new atom type allowed lifting the ambiguity in the definition of angles and

dihedrals, that would have had the same name of the gaff original ones but should have been characterized by a different equilibrium value.

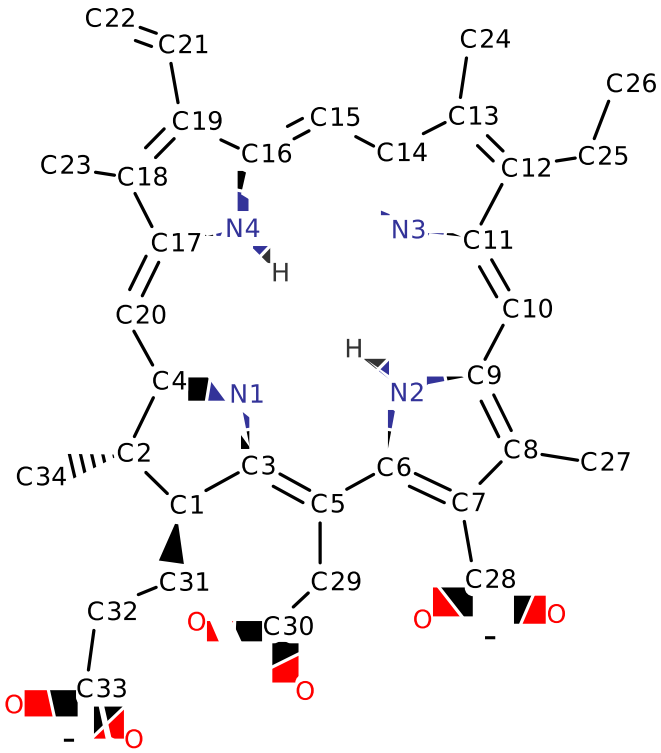

Figure S1: Molecular formula of Ce6, the numbering scheme of the relevant atoms is indicated

In Figure S2 we show the RMSD (root mean square deviation) calculated for all heavy atoms and compared to the QM optimized structure.

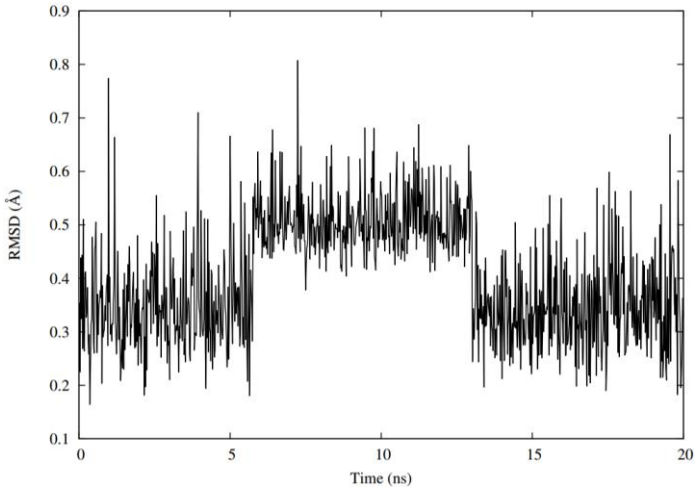

Figure S2: RMSD of Ce6 along the classical MD trajectory.

Hereinafter, for the readers convenience, we give the *mol2* file for Ce6 in its ground state optimized geometry. This file created using the antechamber utility from AmberTools12, contains the atom names, coordinates, gaff atom types and charges, followed by the bonds descriptions.

```
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Ce6
77 81 1 0 0
SMALL
No Charge or Current Charge
@<TRIPOS>ATOM
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2 C2 -2.4310 2.5280 -1.0450 cz 1 Ce6 0.193778
3 C3 -2.0320 0.3030 -0.3190 ce 1 Ce6 0.264087
4 N1 -0.8150 0.9000 -0.3640 ne 1 Ce6 -0.341733
5 C4 -0.9840 2.2130 -0.6800 cf 1 Ce6 0.259458
6 C5 -2.2890 -1.0830 -0.1970 cf 1 Ce6 -0.194062
7 C6 -1.2820 -2.0600 -0.0210 cd 1 Ce6 0.195278
8 C7 -1.3800 -3.5090 0.0900 cc 1 Ce6 -0.165784
9 C8 -0.0970 -4.0030 0.2310 cc 1 Ce6 0.090685
10 C9 0.8200 -2.8950 0.2410 cd 1 Ce6 0.192141
11 N2 0.0620 -1.7570 0.0740 na 1 Ce6 -0.185211
12 C10 2.1970 -2.9870 0.4100 cf 1 Ce6 -0.526319
13 C11 3.1710 -1.9750 0.4540 cc 1 Ce6 0.412952
14 N3 2.9310 -0.6450 0.3020 nc 1 Ce6 -0.410554
15 C12 4.5950 -2.2400 0.6900 cc 1 Ce6 -0.406955
16 C13 5.2100 -1.0150 0.6780 cd 1 Ce6 0.244883
17 C14 4.1530 -0.0380 0.4300 cd 1 Ce6 -0.047967
18 C15 4.3710 1.3400 0.3120 cf 1 Ce6 -0.177306
19 C16 3.4040 2.3050 0.0340 cc 1 Ce6 0.011437
20 N4 2.0730 2.0150 -0.1550 na 1 Ce6 -0.216807
21 C17 1.3650 3.1470 -0.4610 cc 1 Ce6 0.106344
22 C18 2.2920 4.2410 -0.4600 cd 1 Ce6 0.129189
23 C19 3.5560 3.7250 -0.1560 cc 1 Ce6 -0.174478
24 C20 -0.0150 3.2050 -0.7240 cf 1 Ce6 -0.505471
25 C21 4.8330 4.4140 -0.0090 ce 1 Ce6 0.033291
26 C22 5.1840 5.6120 -0.5060 c2 1 Ce6 -0.540887
27 C23 1.9240 5.6750 -0.6990 c3 1 Ce6 -0.285092
28 C24 6.6630 -0.6930 0.8640 c3 1 Ce6 -0.420048
29 C25 5.2230 -3.5950 0.8700 c3 1 Ce6 0.297097
30 C26 5.5170 -4.3200 -0.4580 c3 1 Ce6 -0.267957
31 C27 0.3000 -5.4430 0.3810 c3 1 Ce6 -0.329718
32 C28 -2.6040 -4.4300 0.1310 c 1 Ce6 0.877962
33 O1 -3.3350 -4.3340 1.1530 o 1 Ce6 -0.798185
34 O2 -2.7210 -5.2370 -0.8260 o 1 Ce6 -0.767357
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37 O3 -5.4080 -1.1580 -2.0420 o 1 Ce6 -0.845241
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41 C33 -5.6010 2.8160 2.3820 c 1 Ce6 0.854096
42 O5 -6.2910 3.8670 2.4910 o 1 Ce6 -0.869349
43 O6 -5.4020 1.9410 3.2690 o 1 Ce6 -0.823607
44 H1 -3.9840 0.9810 -1.0440 hc 1 Ce6 0.107692
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```

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46 C34 -2.6220 2.6100 -2.5710 c3 1 Ce6 -0.377481
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50 H6 5.5830 3.8760 0.5690 ha 1 Ce6 0.109283
51 H7 6.1720 6.0190 -0.3140 ha 1 Ce6 0.147010
52 H8 4.5260 6.2120 -1.1260 ha 1 Ce6 0.201300
53 H9 0.8660 5.8600 -0.4950 hc 1 Ce6 0.081898
54 H10 2.5090 6.3400 -0.0540 hc 1 Ce6 0.069854
55 H11 2.1160 5.9860 -1.7350 hc 1 Ce6 0.063205
56 H12 7.2380 -1.5800 1.1470 hc 1 Ce6 0.117835
57 H13 7.1130 -0.2930 -0.0550 hc 1 Ce6 0.098090
58 H14 6.8150 0.0620 1.6450 hc 1 Ce6 0.090821
59 H15 6.1600 -3.4920 1.4310 hc 1 Ce6 -0.044947
60 H16 4.5750 -4.2300 1.4880 hc 1 Ce6 -0.042505
61 H17 5.9650 -5.3040 -0.2740 hc 1 Ce6 0.019606
62 H18 4.6000 -4.4680 -1.0390 hc 1 Ce6 0.082521
63 H19 6.2110 -3.7380 -1.0740 hc 1 Ce6 0.061315
64 H20 1.1530 -5.6950 -0.2610 hc 1 Ce6 0.063415
65 H21 0.5950 -5.6830 1.4120 hc 1 Ce6 0.063282
66 H22 -0.5340 -6.0890 0.1020 hc 1 Ce6 0.129296
67 H23 -3.8790 -2.5050 0.0630 hc 1 Ce6 0.091370
68 H24 -4.3950 -0.8470 0.1890 hc 1 Ce6 0.002891
69 H25 -3.9780 0.7480 1.5320 hc 1 Ce6 0.062520
70 H26 -2.9250 2.1450 1.5850 hc 1 Ce6 -0.022879
71 H27 -4.7510 3.5370 0.5200 hc 1 Ce6 -0.032244
72 H28 -5.7360 2.0960 0.3490 hc 1 Ce6 0.024242
73 H29 -3.6700 2.8160 -2.8150 hc 1 Ce6 0.081178
74 H30 -2.0060 3.4050 -3.0070 hc 1 Ce6 0.051674
75 H31 -2.3430 1.6630 -3.0500 hc 1 Ce6 0.118660
76 H32 1.7170 1.0640 -0.1020 hn 1 Ce6 0.308330
77 H33 0.4170 -0.8090 0.0050 hn 1 Ce6 0.109103

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6 2 45 1
7 2 46 1
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11 5 24 1
12 6 7 1
13 6 35 1
14 7 8 2
15 7 11 1
16 8 9 1
17 8 32 1
18 9 10 2
19 9 31 1
20 10 11 1
21 10 12 1
22 11 77 1
23 12 13 2
24 12 47 1
25 13 14 1
26 13 15 1
27 14 17 2
28 15 16 2
29 15 29 1
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33 18 19 2
34 18 48 1
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81 46 75 1
@<TRIPOS>SUBSTRUCTURE
1 Ce6 1 TEMP 0 **** **** 0 ROOT
```

Hereinafter, the bonded and non-bonded parameters of Ce6 are given as a standard *frcmod* file, obtained employing the *parmchk* utility from AmberTools16.

```
MASS
c3 12.010 0.878
cz 12.010 0.360
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ne 14.010 0.530
cf 12.010 0.360
cd 12.010 0.360
cc 12.010 0.360
na 14.010 0.530
nc 14.010 0.530
c2 12.010 0.360
c 12.010 0.616
o 16.000 0.434
hc 1.008 0.135
ha 1.008 0.135
hn 1.008 0.161

BOND
c3-c3 303.10 1.535
c3-cz 322.50 1.514
c3-ce 331.30 1.505
cz-cf 337.00 1.499
cz-hc 345.80 1.086
c3-hc 337.30 1.092
c3-cf 331.30 1.505
ce-ne 381.80 1.414
ce-cf 562.40 1.338
ne-cf 574.00 1.292
cf-cf 390.50 1.451
cf-cd 387.90 1.453
cd-cc 504.00 1.371
cd-na 438.80 1.371
cc-cc 418.30 1.429
cc-c 377.40 1.462
cc-c3 337.30 1.499
na-hn 406.60 1.011
cf-cc 511.30 1.367
cf-ha 341.50 1.089
cc-nc 431.60 1.376
nc-cd 494.60 1.335
cd-cd 418.30 1.429
cd-c3 337.30 1.499
cc-na 438.80 1.371
cc-ce 387.90 1.453
ce-c2 560.50 1.339
ce-ha 341.50 1.089
c2-ha 344.30 1.087
c -o 648.00 1.214
c3-c 328.30 1.508

ANGLE
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cz-c3-ce 63.881 112.010
cz-c3-c3 63.300 111.820
cz-c3-hc 46.920 110.200
cz-cf-ne 67.260 120.750
```

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c3-c3-hc 46.370 110.050
c3-c3-c3 63.210 110.630
c3-ce-ne 66.960 122.150
c3-ce-cf 64.520 122.110
c3-c3-ce 63.700 111.060
c3-cf-ne 67.260 120.750
c3-cf-cf 63.800 116.990
ce-c3-hc 47.000 110.980
ce-ne-cf 67.330 108.720
ce-cf-cd 64.870 123.930
ce-cf-c3 64.520 122.110
ne-ce-cf 69.730 126.660
ne-cf-cf 69.570 127.620
cf-c3-hc 47.000 110.980
cf-cf-cc 64.810 130.550
cf-cf-ha 47.500 115.900
cf-cd-cc 63.670 128.410
cf-cd-na 66.320 125.920
cf-c3-c 64.020 111.980
cd-cf-c3 63.420 118.220
cd-cc-cc 68.160 114.190
cd-cc-c 65.250 121.420
cd-na-cd 68.940 111.260
cd-na-hn 47.020 125.500
cc-cd-na 72.910 109.420
cc-cc-c3 64.660 115.970
cc-c -o 68.910 125.710
cc-cc-c 63.720 122.690
cc-c3-hc 47.200 110.860
cd-cc-c3 64.810 119.450
cd-cf-cc 63.280 129.000
cd-cf-ha 47.530 115.450
cf-cc-nc 68.220 124.900
cf-cc-cc 65.880 122.590
cc-cf-ha 49.970 115.480
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nc-cc-cc 67.530 121.690
nc-cd-cd 71.150 112.560
nc-cd-cf 67.800 124.530
cc-cd-cd 68.160 114.190
cc-cd-c3 64.810 119.450
cc-c3-c3 63.580 111.890
cd-cd-cf 62.780 127.200
cd-c3-hc 47.200 110.860
cd-cd-c3 64.660 115.970
cf-cc-na 68.820 124.500
cc-na-cc 68.940 109.900
cc-na-hn 47.020 125.500
cc-cc-ce 62.780 127.200
na-cc-cc 72.210 106.800
na-cc-cd 72.910 109.420
cc-cd-cc 67.890 120.230
cd-cc-cf 69.090 117.020
cd-cc-ce 63.670 128.410
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c2-ce-ha 49.560 121.100

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c3-c3-c3-hc 1 4.500 0.000 3.000
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cf-cd-na-hn 1 4.500 180.000 2.000
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cd-cf-c3-c 1 0.000 0.000 2.000
cd-cf-c3-hc 1 0.000 0.000 2.000
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cd-cc-cc-c3 1 4.000 180.000 2.000
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cc-cd-cf-ha 1 6.650 180.000 2.000
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nc-cc-cc-c3 1 4.000 180.000 2.000
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cd-cc-c3-c3 1 0.000 0.000 3.000
cd-cd-cf-cc 1 6.650 180.000 2.000
cd-cd-cf-ha 1 6.650 180.000 2.000
cd-cd-cc-c3 1 4.000 180.000 2.000
cd-cd-c3-hc 1 0.000 0.000 3.000
cd-cf-cc-na 1 6.650 180.000 2.000
cf-cd-cd-c3 1 4.000 180.000 2.000
cf-cc-na-cc 1 4.500 180.000 2.000
cf-cc-na-hn 1 4.500 180.000 2.000
cf-cc-cc-ce 1 4.000 180.000 2.000
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cc-cc-cd-cc 1 4.000 180.000 2.000

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cc-cc-ce-ha 1 4.500 180.000 2.000
na-cc-cf-ha 1 6.650 180.000 2.000
na-cc-cc-cd 1 4.000 180.000 2.000
na-cc-cc-ce 1 4.000 180.000 2.000
na-cc-cd-cc 1 4.000 180.000 2.000
na-cc-cd-c3 1 4.000 180.000 2.000
cc-na-cc-cc 1 4.500 180.000 2.000
cc-cd-cc-ce 1 4.000 180.000 2.000
cd-cc-na-hn 1 4.500 180.000 2.000
cd-cc-cf-ha 1 6.650 180.000 2.000
cd-cc-ce-c2 1 4.500 180.000 2.000
cd-cc-ce-ha 1 4.500 180.000 2.000
cc-cc-na-hn 1 4.500 180.000 2.000
cc-cd-cc-cf 1 4.000 180.000 2.000
cc-ce-c2-ha 1 6.650 180.000 2.000
cf-cf-c3-hc 1 0.000 0.000 2.000
cf-cc-cd-c3 1 4.000 180.000 2.000
ce-cc-cd-c3 1 4.000 180.000 2.000
c3-cd-cc-c3 1 4.000 180.000 2.000
c3-cc-cc-c 1 4.000 180.000 2.000
o -c -c3-hc 1 4.500 0.000 -1.000
o -c -c3-hc 1 4.500 180.000 3.000
c3-c3-c -o 1 0.000 180.000 2.000
c -c3-c3-hc 1 4.500 0.000 3.000
hc-c3-c3-hc 1 4.500 0.000 3.000
ha-ce-c2-ha 1 6.650 180.000 2.000

IMPROPER
cf-cz-cf-ne 1.1 180.0 2.0
c3-cf-ce-ne 1.1 180.0 2.0
c3-cf-cf-ne 1.1 180.0 2.0
c3-cd-cf-ce 1.1 180.0 2.0
cc-cf-cd-na 1.1 180.0 2.0
c -cc-cc-cd 1.1 180.0 2.0
c3-cc-cc-cd 1.1 180.0 2.0
cd-cd-na-hn 1.1 180.0 2.0
cc-cd-cf-ha 1.1 180.0 2.0
cc-cf-cc-nc 1.1 180.0 2.0
c3-cc-cd-cd 1.1 180.0 2.0
cd-cf-cd-nc 1.1 180.0 2.0
cc-cf-cc-na 1.1 180.0 2.0
cc-cc-na-hn 1.1 180.0 2.0
cd-cf-cc-na 1.1 180.0 2.0
c3-cc-cd-cc 1.1 180.0 2.0
cc-cd-cc-ce 1.1 180.0 2.0
cc-cf-cf-ha 1.1 180.0 2.0
c2-cc-ce-ha 1.1 180.0 2.0
ce-ha-c2-ha 1.1 180.0 2.0
cc-o -c -o 1.1 180.0 2.0
c3-o -c -o 1.1 180.0 2.0

NONBON
cz 1.9080 0.0860
c3 1.9080 0.1094
ce 1.9080 0.0860
ne 1.8240 0.1700
cf 1.9080 0.0860
cd 1.9080 0.0860
cc 1.9080 0.0860
na 1.8240 0.1700
nc 1.8240 0.1700
c2 1.9080 0.0860
```

```
c 1.9080 0.0860
o 1.6612 0.2100
hc 1.4870 0.0157
ha 1.4590 0.0150
hn 0.6000 0.0157
```