Electronic Supplementary Information

Antiparallel Alignment of the Two Angular Momenta in a Photoexcited Dysprosium-Phthalocyanine complex.

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Figure S1. Absorption (top) and MCD (bottom) spectra of [DyPc(cyclen)]Cl doped in a PMMA film measured at 1.5 K under a magnetic field of 1 T.

Figure S2. Result of band deconvolution of absorption (top) and MCD (bottom) spectra of [DyPc(cyclen)]Cl doped in a PMMA film measured at 100 K under a magnetic field of 1 T. Observed spectra are shown in solid line (green). *A*-term components are shown in thick broken line (red) and *B*-term components in thick broken line (black). The sum of these components is shown in dotted line (blue). All spectra have been scaled so that the absorbance at the maxima of the Q band is set to 1.
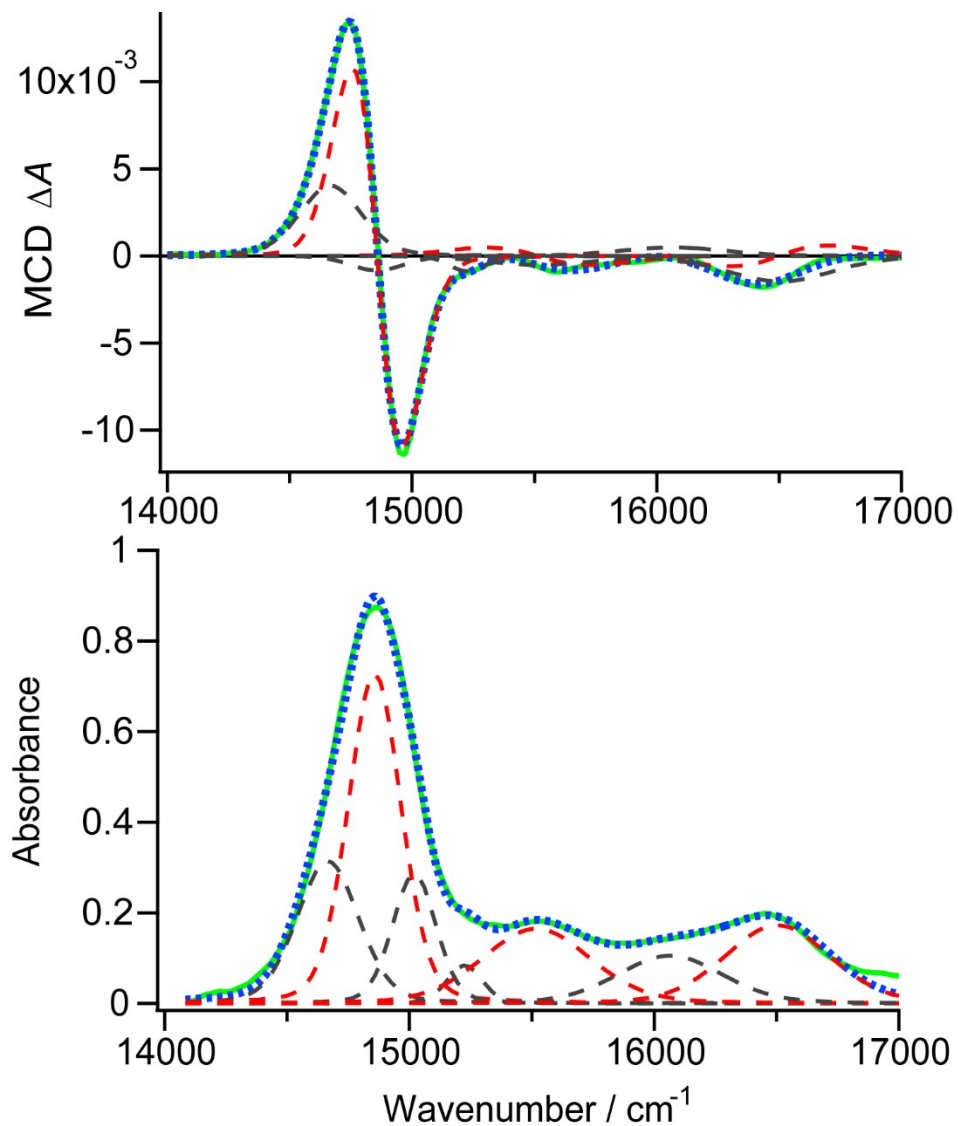
Figure S3. Result of band deconvolution of absorption (top) and MCD (bottom) spectra of [DyPc(cyclen)]Cl doped in a PMMA film measured at 1.5 K under a magnetic field of 1 T. Observed spectra are shown in solid line (green). *A*-term components are shown in thick broken line (red) and *B*-term components in thick broken line (black). The sum of these components is shown in dotted line (blue). All spectra have been scaled so that the absorbance at the maxima of the Q band is set to 1.
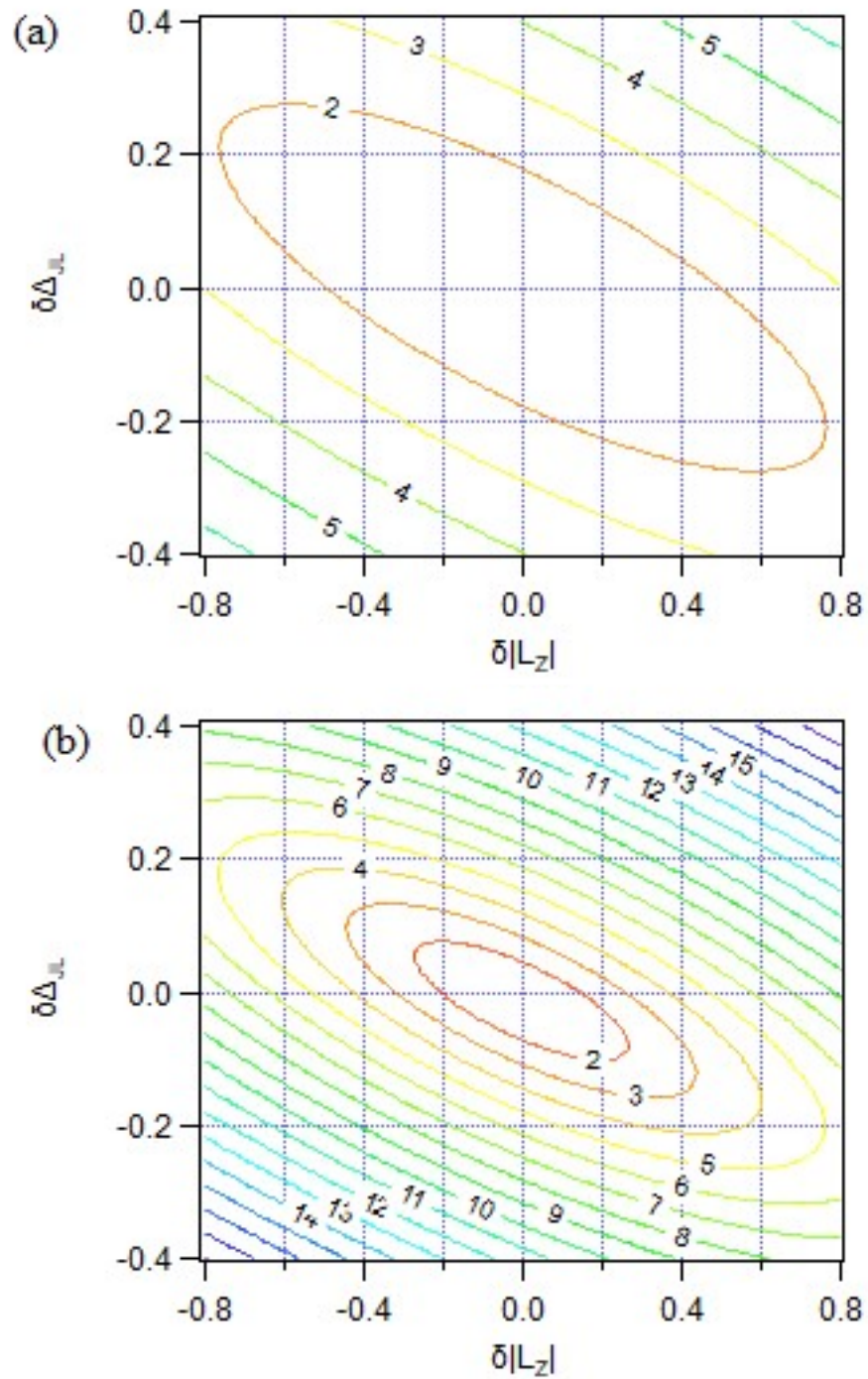
Figure S4. Contour maps of the ratio RMS1/RMS0 of simulation 1 (a, $J_z = 11/2$) and simulation 2 (b, $J_z = 13/2$), where RMS0 is the minimum RMS error obtained with the two parameters ($|L_z|$ and Δ_{JL}) determined by means of least-square procedure, and RMS1 is the RMS error obtained varying two parameters if the two by the values indicated in the vertical and horizontal axes.
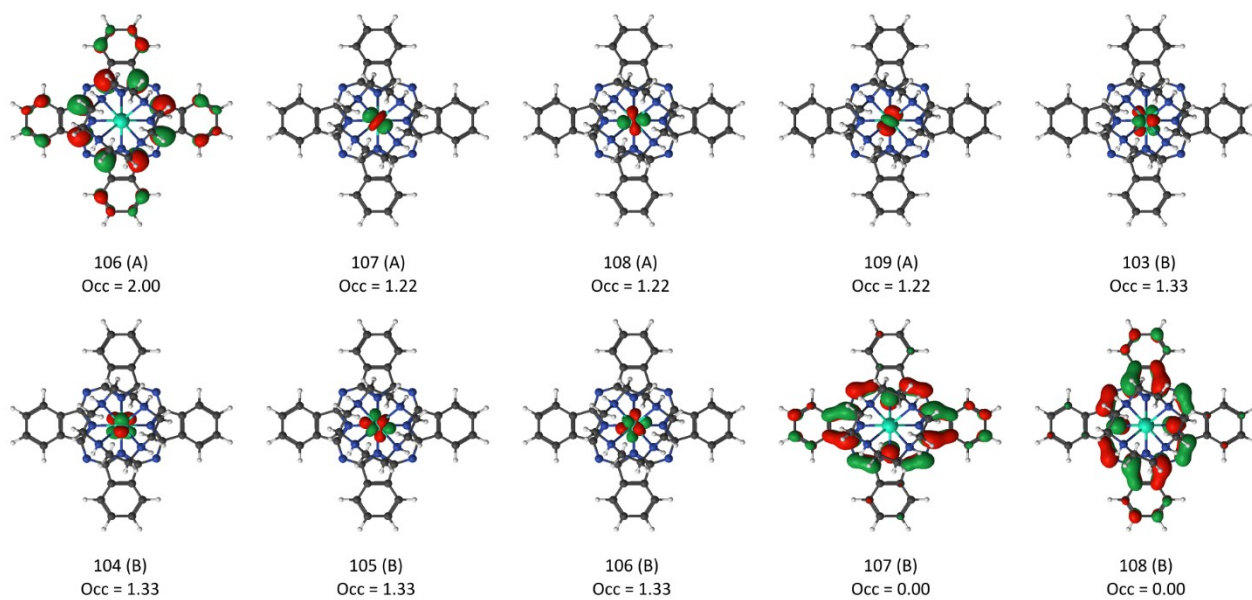
Figure S5. Molecular orbital of [DyPc(cyclen)]$^+$ obtained from RASSCF(9,7) calculations with 9 configurations of *A* symmetry.
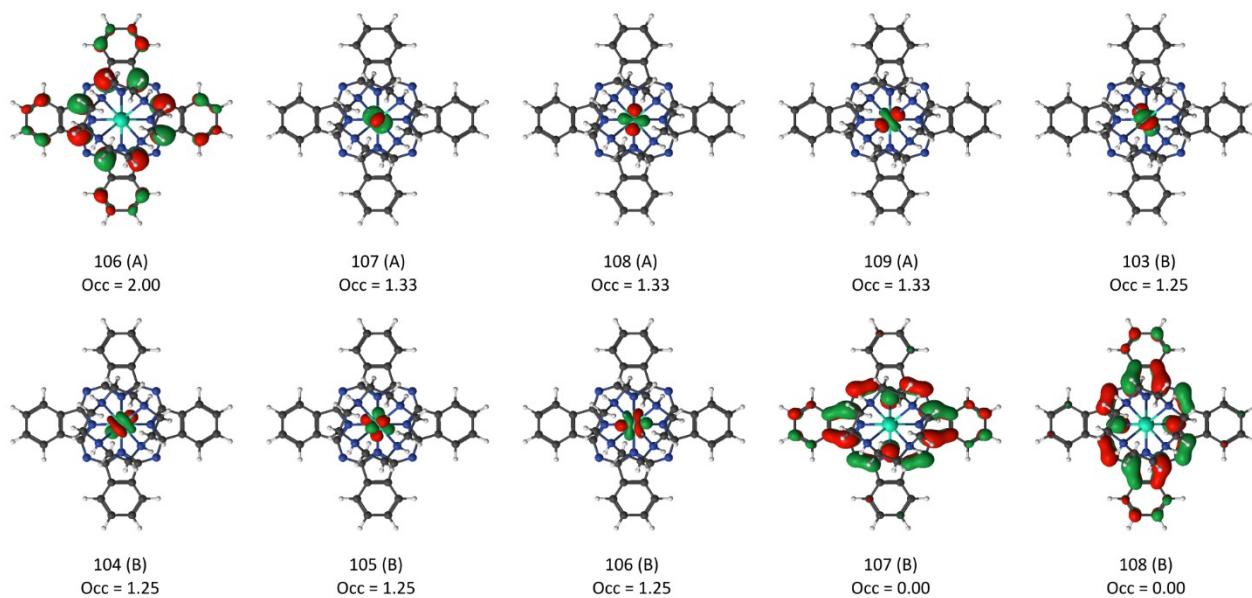
Figure S6. Molecular orbital of [DyPc(cyclen)]$^+$ obtained from RASSCF(9,7) calculations with 12 configurations of *B* symmetry.

106 (A)
Occ = 2.00

107 (A)
Occ = 1.14

108 (A)
Occ = 1.12

109 (A)
Occ = 1.00

103 (B)
Occ = 1.50

104 (B)
Occ = 1.50

105 (B)
Occ = 1.37

106 (B)
Occ = 1.37

107 (B)
Occ = 0.00

108 (B)
Occ = 0.00
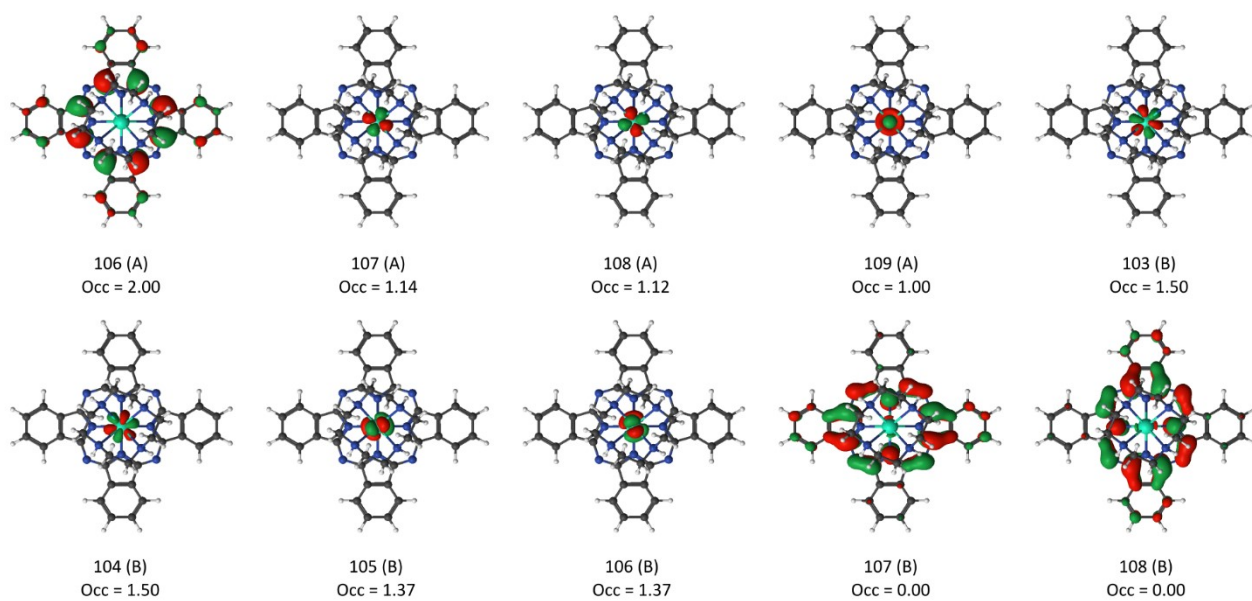
Figure S7. Orbital shapes for the doublet 2 of [DyPc(cyclen)]$^+$ under C_2 symmetry with basis set 1.

106 (A)
Occ = 2.00

107 (A)
Occ = 1.47

108 (A)
Occ = 1.23

109 (A)
Occ = 1.13

103 (B)
Occ = 1.35

104 (B)
Occ = 1.35

105 (B)
Occ = 1.24

106 (B)
Occ = 1.24

107 (B)
Occ = 0.00

108 (B)
Occ = 0.00
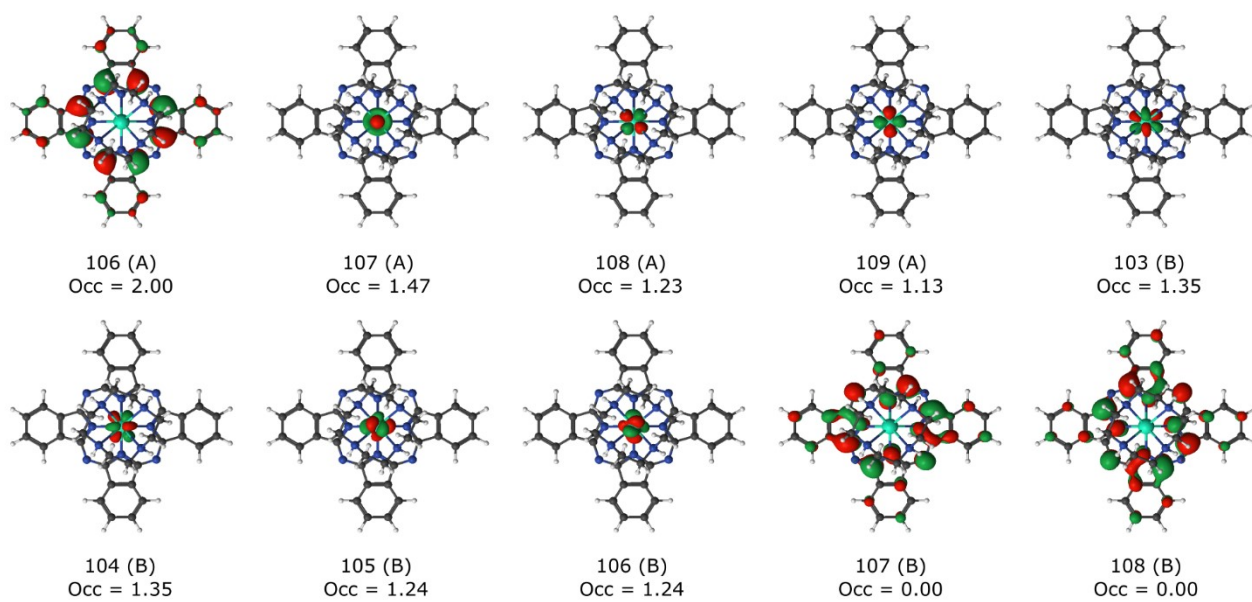
Figure S8. Orbital shapes for the doublet 3 of [DyPc(cyclen)]$^+$ under C_2 symmetry with basis set 1.

Orbital panels (top block):

106 (A) Occ = 2.00   107 (A) Occ = 1.51   108 (A) Occ = 1.35   109 (A) Occ = 1.16   103 (B) Occ = 1.26

104 (B) Occ = 1.26   105 (B) Occ = 1.23   106 (B) Occ = 1.23   107 (B) Occ = 0.00   108 (B) Occ = 0.00
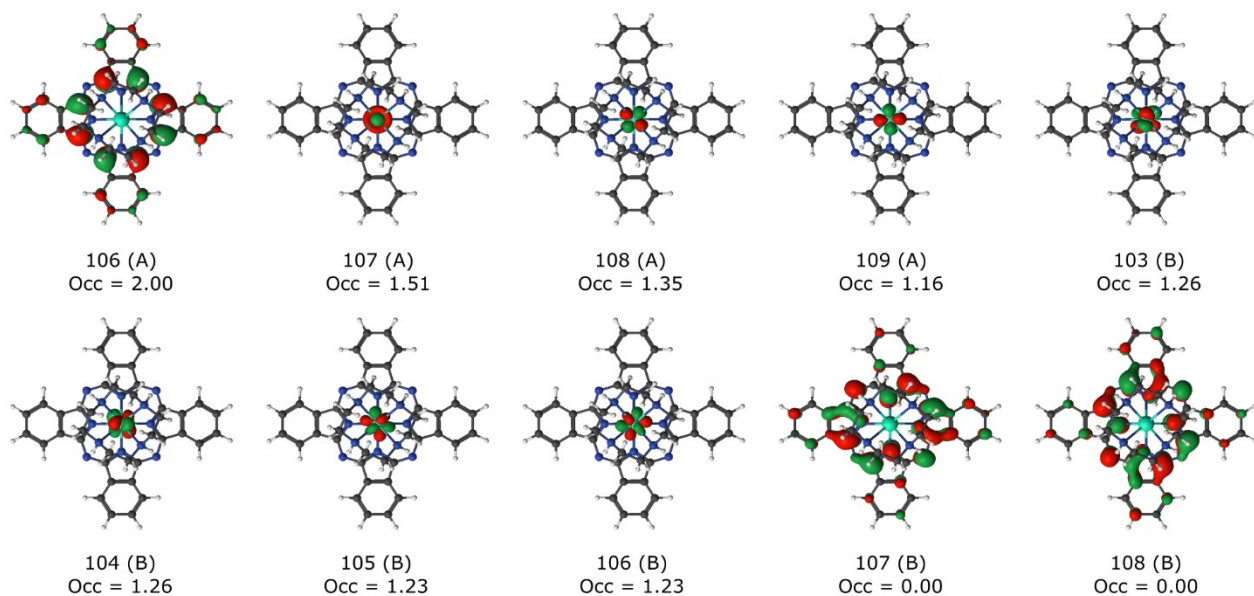
Figure S9. Orbital shapes for the doublet 4 of [DyPc(cyclen)]$^+$ under C_2 symmetry with basis set 1.

Orbital panels (bottom block):

106 (A) Occ = 2.00   107 (A) Occ = 1.50   108 (A) Occ = 1.49   109 (A) Occ = 1.00   103 (B) Occ = 1.50

104 (B) Occ = 1.50   105 (B) Occ = 1.00   106 (B) Occ = 1.00   107 (B) Occ = 0.00   108 (B) Occ = 0.00
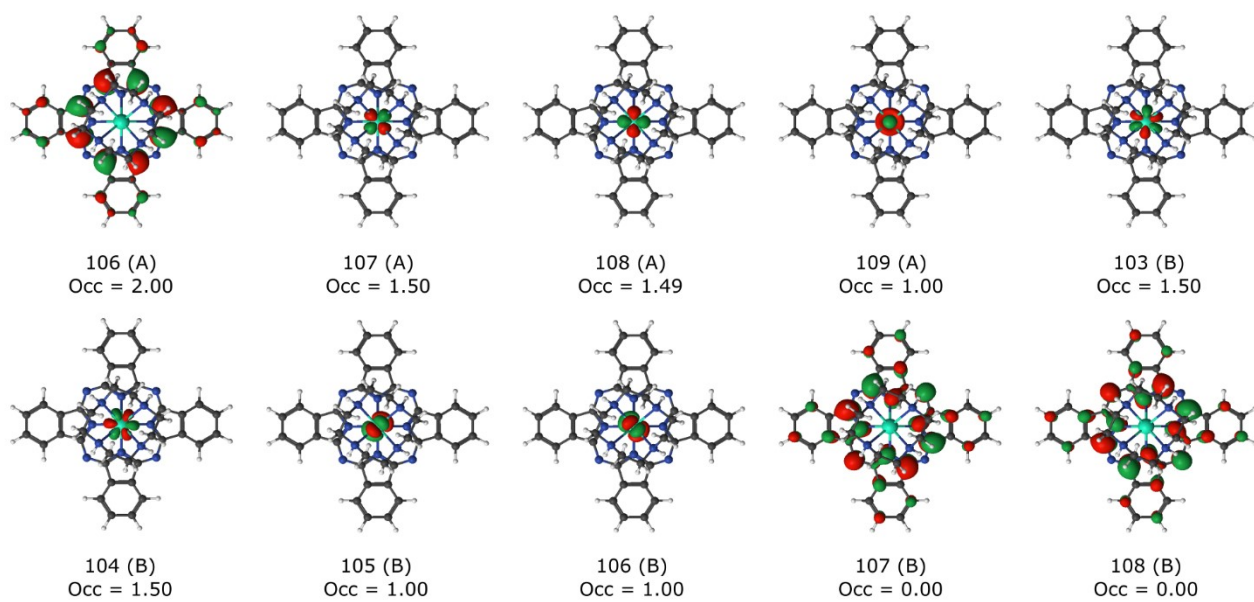
Figure S10. Orbital shapes for the doublet 8 of [DyPc(cyclen)]$^+$ under C_2 symmetry with basis set 1.

106 (A)
Occ = 1.17

107 (A)
Occ = 1.15

108 (A)
Occ = 1.01

109 (A)
Occ = 1.00

103 (B)
Occ = 1.50

104 (B)
Occ = 1.50

105 (B)
Occ = 1.34

106 (B)
Occ = 1.34

107 (B)
Occ = 0.55

108 (B)
Occ = 0.45
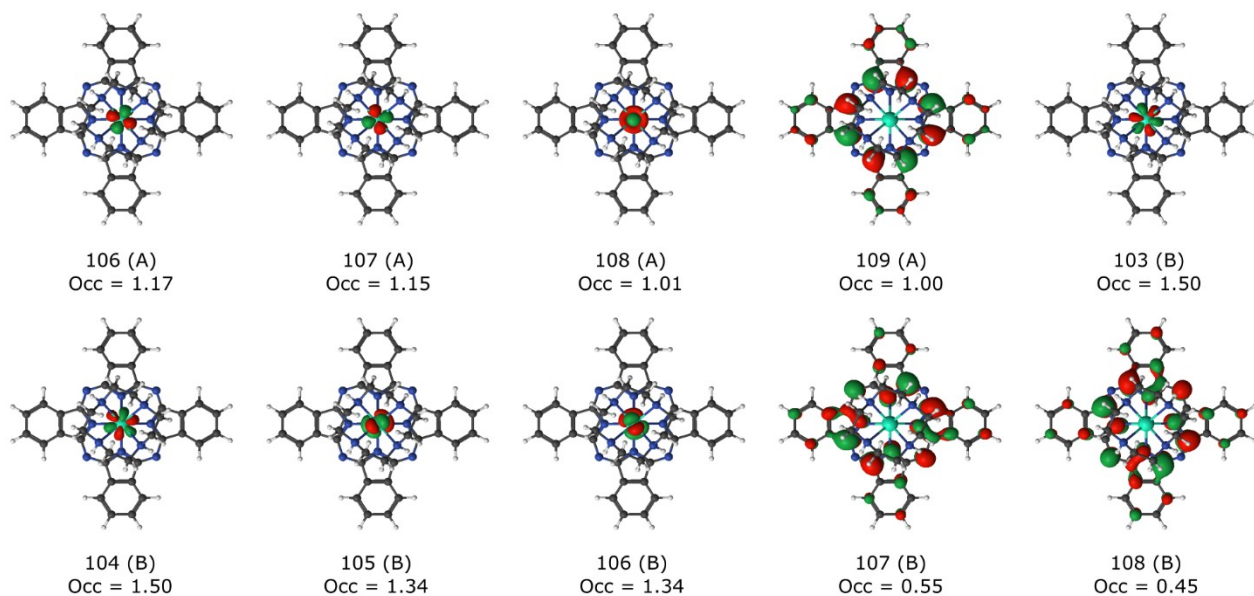
Figure S11. Orbital shapes for the doublet 163 of [DyPc(cyclen)]$^+$ under C_2 symmetry with basis set 1.

106 (A)
Occ = 1.18

107 (A)
Occ = 1.15

108 (A)
Occ = 1.00

109 (A)
Occ = 1.00

103 (B)
Occ = 1.50

104 (B)
Occ = 1.50

105 (B)
Occ = 1.34

106 (B)
Occ = 1.33

107 (B)
Occ = 0.55

108 (B)
Occ = 0.45
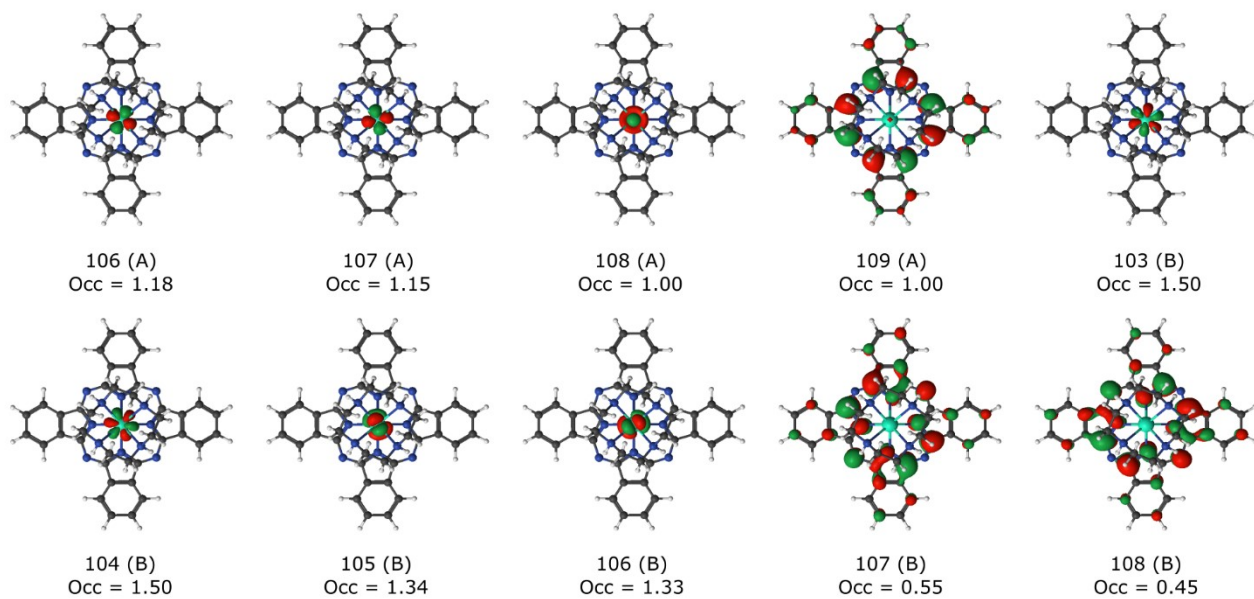
Figure S12. Orbital shapes for the doublet 164 of [DyPc(cyclen)]$^+$ under C_2 symmetry with basis set 1.

106 (A)
Occ = 1.53

107 (A)
Occ = 1.46

108 (A)
Occ = 1.01

109 (A)
Occ = 1.00

103 (B)
Occ = 1.50

104 (B)
Occ = 1.50

105 (B)
Occ = 1.00

106 (B)
Occ = 1.00

107 (B)
Occ = 0.50

108 (B)
Occ = 0.50
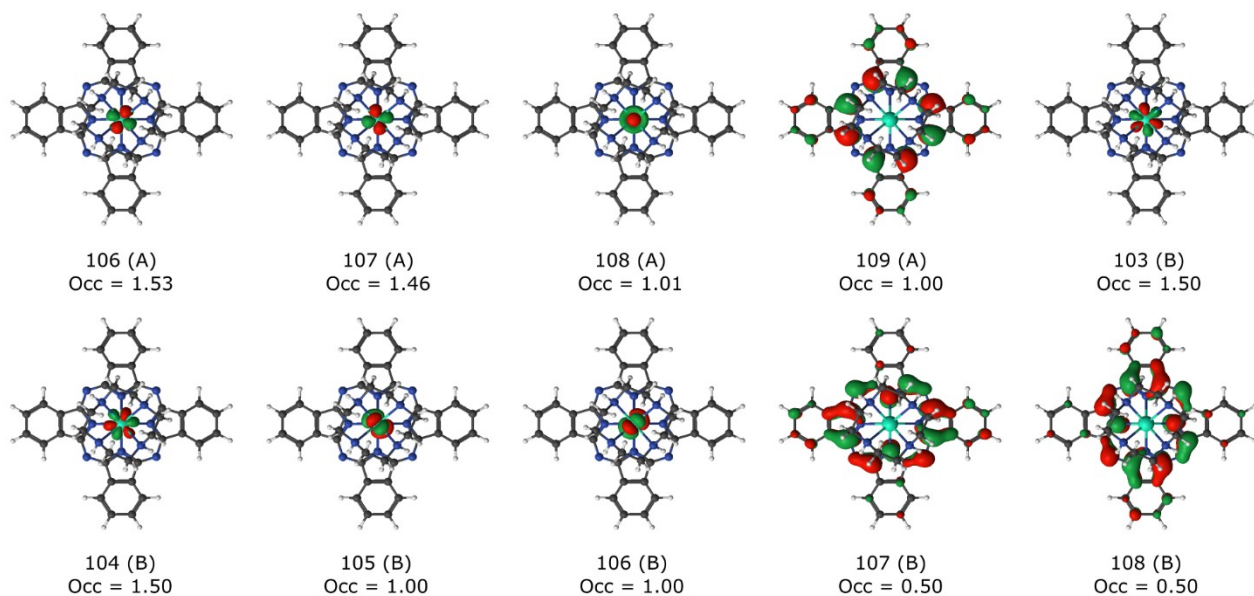
Figure S13. Orbital shapes for the doublet 165 of [DyPc(cyclen)]$^+$ under C_2 symmetry with basis set 1.

106 (A)
Occ = 1.52

107 (A)
Occ = 1.46

108 (A)
Occ = 1.01

109 (A)
Occ = 1.00

103 (B)
Occ = 1.50

104 (B)
Occ = 1.49

105 (B)
Occ = 1.01

106 (B)
Occ = 1.01

107 (B)
Occ = 0.50

108 (B)
Occ = 0.50
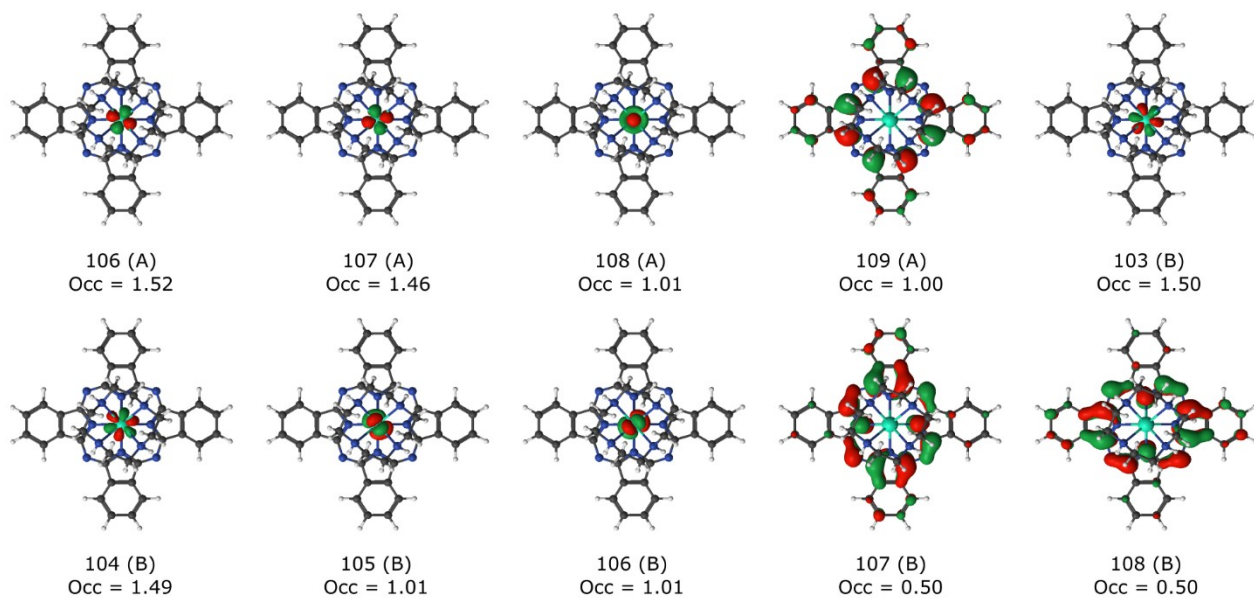
Figure S14. Orbital shapes for the doublet 166 of [DyPc(cyclen)]$^+$ under C_2 symmetry with basis set 1.

106 (A)
Occ = 1.27

107 (A)
Occ = 1.15

108 (A)
Occ = 1.08

109 (A)
Occ = 1.00

103 (B)
Occ = 1.44

104 (B)
Occ = 1.44

105 (B)
Occ = 1.31

106 (B)
Occ = 1.31

107 (B)
Occ = 0.50

108 (B)
Occ = 0.50
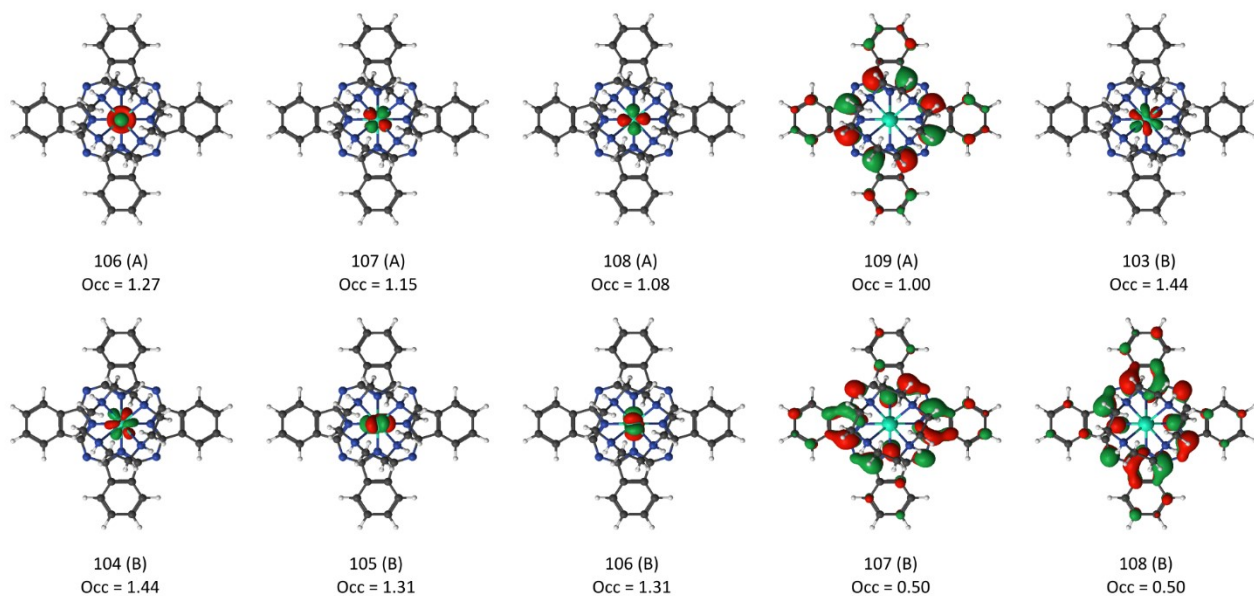
Figure S15. Orbital shapes for the doublet 167 of [DyPc(cyclen)]$^+$ under C_2 symmetry with basis set 1.

106 (A)
Occ = 1.27

107 (A)
Occ = 1.15

108 (A)
Occ = 1.08

109 (A)
Occ = 1.00

103 (B)
Occ = 1.44

104 (B)
Occ = 1.44

105 (B)
Occ = 1.31

106 (B)
Occ = 1.31

107 (B)
Occ = 0.50

108 (B)
Occ = 0.50
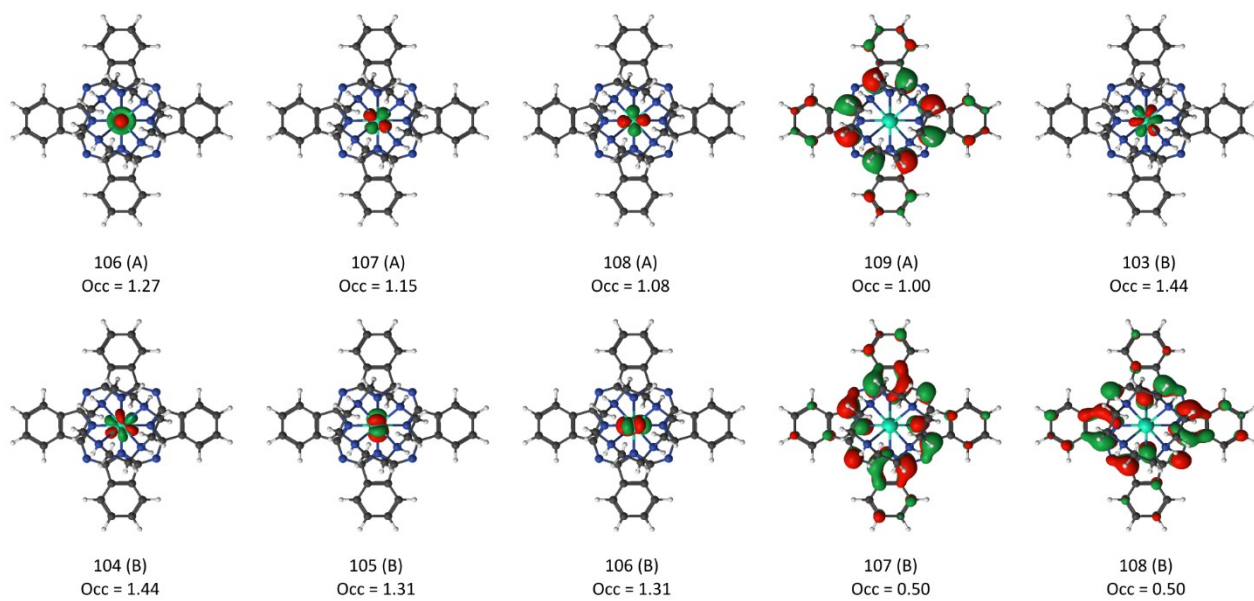
Figure S16. Orbital shapes for the doublet 168 of [DyPc(cyclen)]$^+$ under C_2 symmetry with basis set 1.

106 (A)
Occ = 1.48

107 (A)
Occ = 1.22

108 (A)
Occ = 1.11

109 (A)
Occ = 1.00

103 (B)
Occ = 1.35

104 (B)
Occ = 1.35

105 (B)
Occ = 1.25

106 (B)
Occ = 1.23

107 (B)
Occ = 0.88

108 (B)
Occ = 0.12
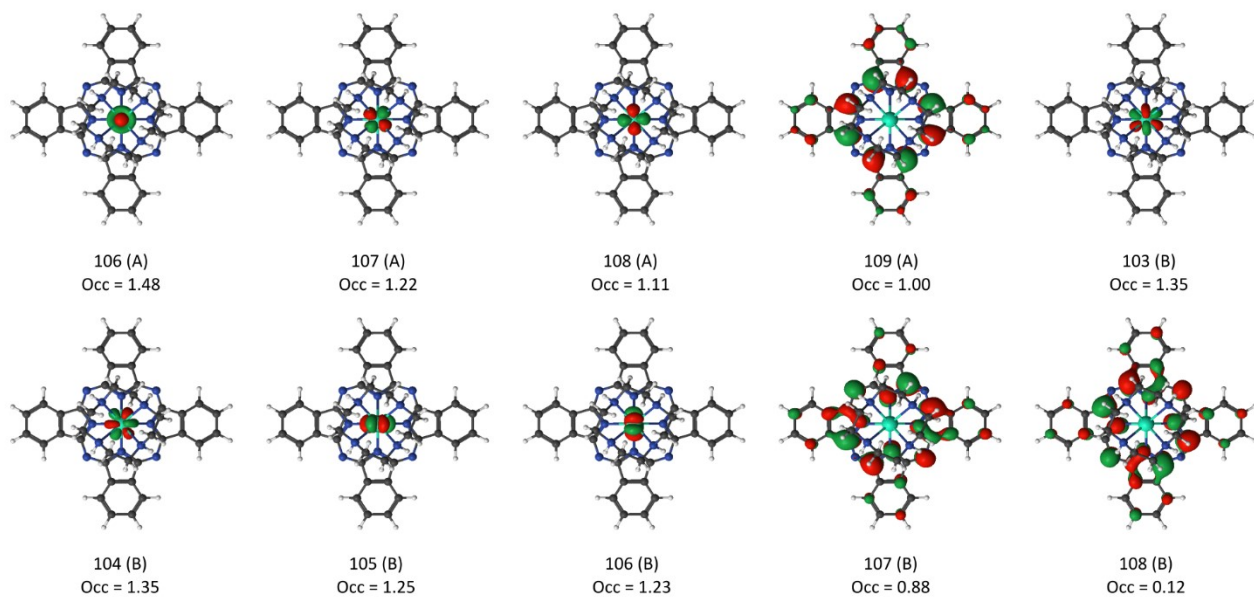
Figure S17. Orbital shapes for the doublet 169 of [DyPc(cyclen)]$^+$ under C_2 symmetry with basis set 1.

106 (A)
Occ = 1.48

107 (A)
Occ = 1.23

108 (A)
Occ = 1.11

109 (A)
Occ = 1.00

103 (B)
Occ = 1.35

104 (B)
Occ = 1.35

105 (B)
Occ = 1.25

106 (B)
Occ = 1.23

107 (B)
Occ = 0.88

108 (B)
Occ = 0.12
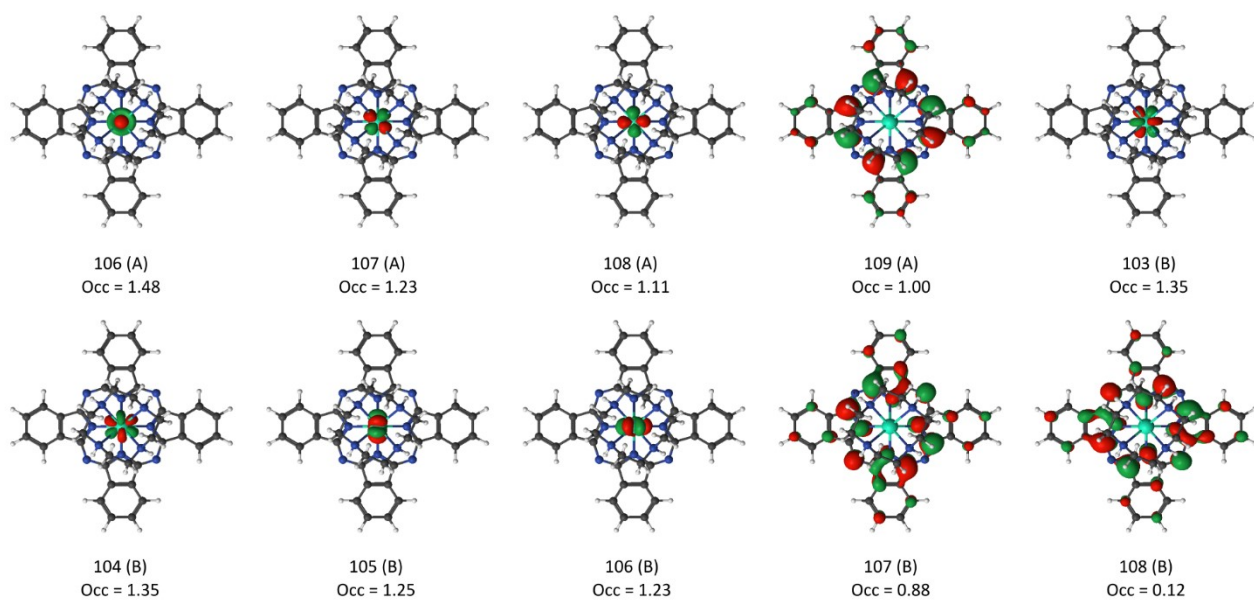
Figure S18. Orbital shapes for the doublet 170 of [DyPc(cyclen)]$^+$ under C_2 symmetry with basis set 1.

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106 (A)
Occ = 1.54

107 (A)
Occ = 1.29

108 (A)
Occ = 1.11

109 (A)
Occ = 1.00

103 (B)
Occ = 1.32

104 (B)
Occ = 1.31

105 (B)
Occ = 1.22

106 (B)
Occ = 1.22

107 (B)
Occ = 0.56

108 (B)
Occ = 0.44
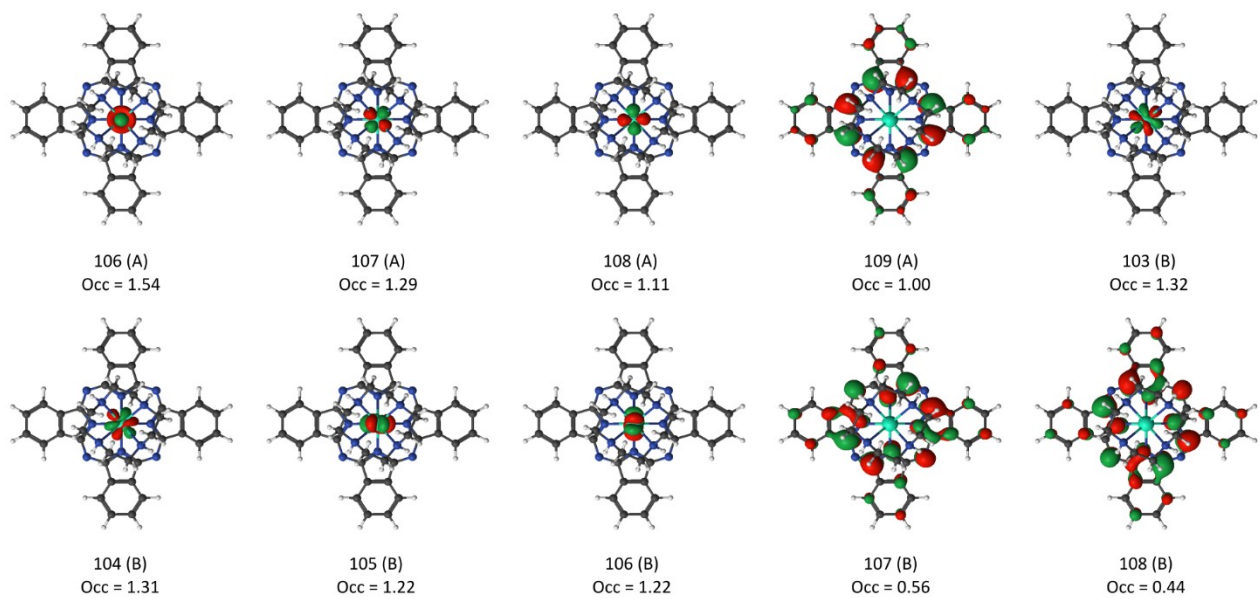
Figure S19. Orbital shapes for the doublet 171 of $[DyPc(cyclen)]^+$ under C_2 symmetry with basis set 1.

106 (A)
Occ = 1.54

107 (A)
Occ = 1.28

108 (A)
Occ = 1.12

109 (A)
Occ = 1.00

103 (B)
Occ = 1.32

104 (B)
Occ = 1.32

105 (B)
Occ = 1.21

106 (B)
Occ = 1.21

107 (B)
Occ = 0.56

108 (B)
Occ = 0.44
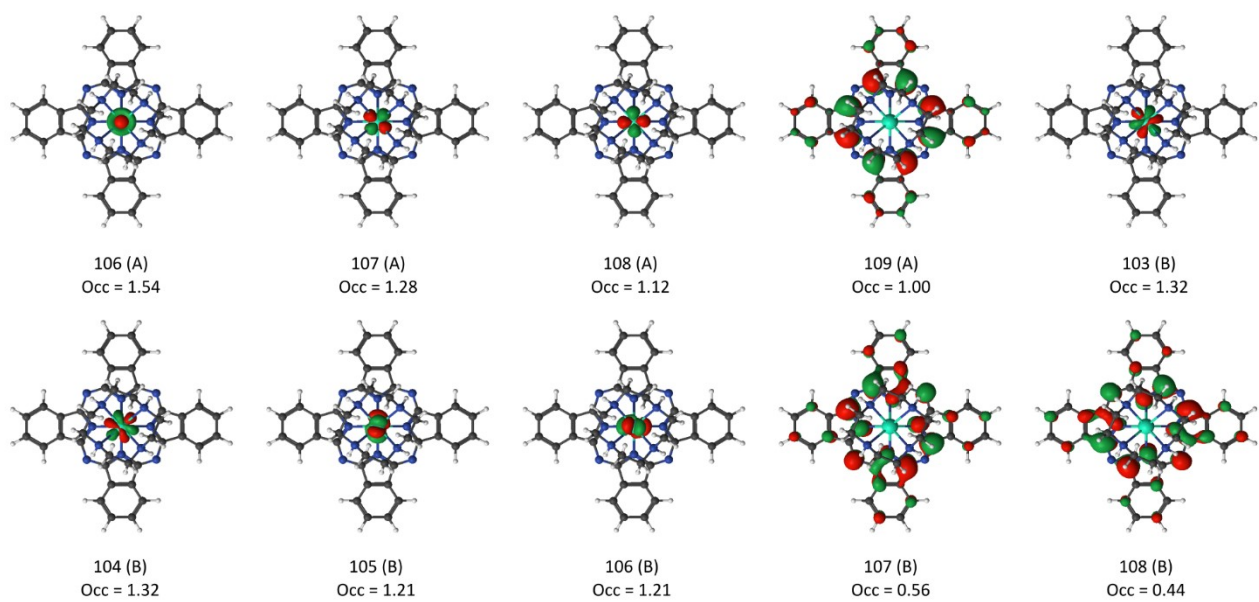
Figure S20. Orbital shapes for the doublet 172 of $[DyPc(cyclen)]^+$ under C_2 symmetry with basis set 1.

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Table S1. Parameters determined by the band deconvolution of absorption and MCD spectra of [DyPc(cyclen)]Cl doped in a PMMA film.

	Band1		Band2	Band3	Band4	Band5		Band6	Band7	
E_0 (cm^{-1})[a]	14666		14857	15019	15226	15515		16062	16501	
Γ (cm^{-1})[a]	298		254	210	170	523		507	506	
η[a]	0.26		0.26	0.26	0.26	0.26		0.26	0.26	
D_0	5.2		10	3.3	0.77	4.6		2.7	4.3	

Values obtained by measurements under a fixed magnetic field at 1 T

T (K)	B_0/D_0	A_1/D_0	B_0/D_0	B_0/D_0	B_0/D_0	A_1/D_0	B_0/D_0	B_0/D_0	A_1/D_0	B_0/D_0
100	-0.045	13	-0.027	0.032	0.0046	3.0	0.010	-0.0055	-3.1	0.025
1.5	0.14	-60	-0.025	0.0028	-0.017	-11	-0.030	0.027	12	-0.079

Values obtained by measurements at 1.5 K

B (T)	B_0/D_0	A_1/D_0	B_0/D_0	B_0/D_0	B_0/D_0	A_1/D_0	B_0/D_0	B_0/D_0	A_1/D_0	B_0/D_0
0.2	0.42	-168	0.029	-0.090	-0.052	-31	-0.096	0.069	33	-0.24
0.4	0.31	-128	0.030	-0.062	-0.038	-25	-0.075	0.054	25	-0.19
0.6	0.26	-96	-0.027	-0.033	-0.028	-18	-0.054	0.040	19	-0.14
0.8	0.18	-75	-0.021	-0.011	-0.022	-14	-0.040	0.032	15	-0.10
2	0.056	-24	-0.035	0.021	-0.0067	-4.1	-0.011	0.011	4.5	-0.027
3	0.025	-11	-0.040	0.026	-0.0030	-1.6	-0.0034	0.0043	1.8	-0.0087
4	0.0077	-4.1	-0.040	0.030	-0.00095	-0.26	-0.00058	0.0018	0.60	0.00088
5	-0.0026	-0.28	-0.041	0.033	0.00016	0.52	0.0019	-0.00015	-0.26	0.0064
6	-0.0086	2.6	-0.041	0.034	0.00092	1.0	0.0034	-0.0013	-0.79	0.010

a) E_0, Γ, η are the parameters defining the normalized pseudo-Voigt function,

$$f(E) = (1 - \eta)f_G(E;E_0,\gamma_G) + \eta f_L(E;E_0,\gamma_L)$$

where $f_G(E;E_0,\gamma_G)$ and $f_L(E;E_0,\gamma_L)$ are the normalized Gaussian and Lorentzian function,

$$f_G(E;E_0,\gamma_G) = \left(\frac{1}{\sqrt{\pi}\gamma_G}\right)\exp\left(-\frac{(E - E_0)^2}{\gamma_G^2}\right)$$

$$f_L(E;E_0,\gamma_L) = \left(\frac{1}{\gamma_L}\right)\left(1 + \frac{(E - E_0)^2}{\gamma_L^2}\right)^{-1}$$

with $\Gamma = 2\sqrt{ln2}\gamma_G = 2\gamma_L$.

Details of *ab initio* calculations.

All calculations such as SCF, RASSCF, RASSI and SINGLE_ANISO were performed on Open Molcas v.22.06 with the employment of two groups of basis sets. The employed basis sets are as follows.

Basis set 1	Basis set 2
Dy = ANO-RCC…9s8p6d4f3g2h	Dy = ANO-RCC…8s7p5d3f2g1h
N_{close} = ANO-RCC…3s2p1d	N_{close} = ANO-RCC…3s2p1d
$N_{distant}$ = ANO-RCC…2s1p	$N_{distant}$ = ANO-RCC…2s1p
C_{close} = ANO-RCC…2s1p	C_{close} = ANO-RCC…2s1p
$C_{distant}$ = ANO-RCC…2s1p	$C_{distant}$ = ANO-RCC…2s1p
H = ANO-RCC…1s	H = ANO-RCC…1s

Table S2. Selected dipole transition strengths for [DyPc(cyclen)]$^{+}$ as extracted from RASSCF/RASSI/SINGLE_ANISO calculations , RAS(1,7,2).

Basis Set 1						
From	To	Oscillator Strength	Einstein Coefficients (sec^{-1})			Total A (sec^{-1})
			A_x	A_y	A_z	
1	333	2.50	7.63×10^8	7.61×10^8	0.00	1.52×10^9
2	334	2.50	7.63×10^8	7.61×10^8	0.00	1.52×10^9
1	335	2.52	7.65×10^8	7.67×10^8	0.00	1.53×10^9
2	336	2.52	7.65×10^8	7.67×10^8	0.00	1.53×10^9
3	326	2.56	7.71×10^8	7.71×10^8	0.00	1.54×10^9
4	325	2.56	7.71×10^8	7.71×10^8	0.00	1.54×10^9
3	328	2.58	7.76×10^8	7.76×10^8	0.00	1.55×10^9
4	327	2.58	7.76×10^8	7.76×10^8	0.00	1.55×10^9
5	337	2.48	7.60×10^8	7.51×10^8	0.00	1.51×10^9
6	338	2.48	7.60×10^8	7.51×10^8	0.00	1.51×10^9
5	339	2.48	7.50×10^8	7.59×10^8	0.00	1.51×10^9
6	340	2.48	7.50×10^8	7.59×10^8	0.00	1.51×10^9
7	342	2.06	6.48×10^8	6.48×10^8	0.00	1.30×10^9
8	341	2.06	6.48×10^8	6.48×10^8	0.00	1.30×10^9
7	343	2.04	6.43×10^8	6.43×10^8	0.00	1.29×10^9
8	344	2.04	6.43×10^8	6.43×10^8	0.00	1.29×10^9
9	345	1.61	5.31×10^8	5.33×10^8	0.00	1.06×10^9
10	346	1.61	5.31×10^8	5.33×10^8	0.00	1.06×10^9
9	347	1.60	5.30×10^8	5.28×10^8	0.00	1.06×10^9
10	348	1.60	5.30×10^8	5.28×10^8	0.00	1.06×10^9
12	361	0.36	1.34×10^8	1.33×10^8	0.00	2.67×10^8
11	362	0.36	1.34×10^8	1.33×10^8	0.00	2.67×10^8
12	363	0.37	1.34×10^8	1.35×10^8	0.00	2.69×10^8
11	364	0.37	1.34×10^8	1.35×10^8	0.00	2.69×10^8
14	369	0.83	3.33×10^8	3.35×10^8	0.00	6.68×10^8
13	370	0.83	3.33×10^8	3.35×10^8	0.00	6.68×10^8
14	371	0.98	3.96×10^8	3.94×10^8	0.00	7.90×10^8
13	372	0.98	3.96×10^8	3.94×10^8	0.00	7.90×10^8
15	329	2.44	7.18×10^8	7.18×10^8	0.00	1.44×10^9
16	330	2.44	7.18×10^8	7.18×10^8	0.00	1.44×10^9
15	331	2.43	7.14×10^8	7.14×10^8	0.00	1.43×10^9

From	To	Oscillator Strength	A_x	A_y	A_z	Total A (sec^{-1})
16	332	2.43	7.14×10^8	7.14×10^8	0.00	1.43×10^9

Basis Set 2						
From	To	Oscillator Strength	Einstein Coefficients (sec^{-1})			Total A (sec^{-1})
			A_x	A_y	A_z	
1	333	2.52	7.72×10^8	7.74×10^8	0.00	1.55×10^9
2	334	2.52	7.72×10^8	7.74×10^8	0.00	1.55×10^9
1	335	2.53	7.79×10^8	7.76×10^8	0.00	1.55×10^9
2	336	2.53	7.79×10^8	7.76×10^8	0.00	1.55×10^9
3	325	2.58	7.83×10^8	7.83×10^8	0.00	1.57×10^9
4	326	2.58	7.83×10^8	7.83×10^8	0.00	1.57×10^9
3	328	2.59	7.88×10^8	7.88×10^8	0.00	1.58×10^9
4	327	2.59	7.88×10^8	7.88×10^8	0.00	1.58×10^9
5	338	2.50	7.66×10^8	7.70×10^8	0.00	1.54×10^9
6	337	2.50	7.66×10^8	7.70×10^8	0.00	1.54×10^9
5	340	2.50	7.69×10^8	7.65×10^8	0.00	1.53×10^9
6	339	2.50	7.69×10^8	7.65×10^8	0.00	1.53×10^9
7	341	2.07	6.57×10^8	6.57×10^8	0.00	1.31×10^9
8	342	2.07	6.57×10^8	6.57×10^8	0.00	1.31×10^9
7	344	2.06	6.52×10^8	6.52×10^8	0.00	1.30×10^9
8	343	2.06	6.52×10^8	6.52×10^8	0.00	1.30×10^9
10	345	1.62	5.41×10^8	5.40×10^8	0.00	1.08×10^9
9	346	1.62	5.41×10^8	5.40×10^8	0.00	1.08×10^9
10	347	1.61	5.37×10^8	5.38×10^8	0.00	1.07×10^9
9	348	1.61	5.37×10^8	5.38×10^8	0.00	1.07×10^9
11	361	0.37	1.35×10^8	1.35×10^8	0.00	2.69×10^8
12	362	0.37	1.35×10^8	1.35×10^8	0.00	2.69×10^8
12	363	0.37	1.36×10^8	1.35×10^8	0.00	2.71×10^8
11	364	0.37	1.36×10^8	1.35×10^8	0.00	2.71×10^8
13	369	0.84	3.41×10^8	3.41×10^8	0.00	6.82×10^8
14	370	0.84	3.41×10^8	3.41×10^8	0.00	6.82×10^8
13	371	0.99	4.00×10^8	4.00×10^8	0.00	8.01×10^8
14	372	0.99	4.00×10^8	4.00×10^8	0.00	8.01×10^8
15	330	2.45	7.26×10^8	7.27×10^8	0.00	1.45×10^9
16	329	2.45	7.26×10^8	7.27×10^8	0.00	1.45×10^9
15	331	2.44	7.23×10^8	7.23×10^8	0.00	1.45×10^9
16	332	2.44	7.23×10^8	7.23×10^8	0.00	1.45×10^9

Table S3. The calculated transition energy, orbital and spin angular momenta of the ground doublet and the excited doublet SO states for [DyPc(cyclen)]$^+$, generated from RAS(1,7,2) calculation with basis set 2.

Doublet	Spin-orbit State	Energy (cm^{-1})	Oscillator Strength (initial doublet → final doublet)	$|L_z|$	$|S_z|$	$|J_z|$ $= |L_z + S_z|$	Change in $|J_z|$ from the initial doublet	Primal $|J_z\rangle$	Δ_{JL}
1	1, 2	0.000		3.62	1.83	5.45		$|\pm 11/2\rangle$	
2	3, 4	29.452		4.22	2.23	6.45		$|\pm 13/2\rangle$	
3	5, 6	74.986		2.79	1.33	4.12		$|\pm 9/2\rangle$	
4	7, 8	142.043		1.88	0.90	2.78		$|\pm 7/2\rangle$	
8	15, 16	416.164		4.94	2.48	7.42		$|\pm 15/2\rangle$	
163	325, 326	30197.769	2.56 (2→163)	2.18	2.17	4.35	−2.10		−6.56
164	327, 328	30210.877	2.56 (2→164)	6.43	2.17	8.60	2.15		
165	329, 330	30242.648	2.44 (8→165)	7.03	2.47	9.50	2.08		5.14
166	331, 332	30252.926	2.43 (8→166)	2.79	2.46	5.25	−2.17		
167	333, 334	30331.760	2.50 (1→167)	1.54	1.75	3.29	−2.16		−1.55
168	335, 336	30334.863	2.52 (1→168)	5.65	1.77	7.42	1.97		
169	337, 338	30398.958	2.48 (3→169)	4.89	1.42	6.31	2.19		0.65
170	339, 340	30400.252	2.48 (3→170)	0.83	1.39	2.22	−1.90		
171	341, 342	30980.705	2.06 (4→171)	0.55	0.69	1.24	−1.54		−3.43
172	343, 344	30987.569	2.04 (4→172)	4.71	0.71	5.42	2.64		