Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Detection of weak ring current in a cyclic porphyrin nanoring using magnetic circular dichroism

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Supporting Information

Tables with calculated transition energies, oscillator strengths, Faraday parameters, and polarization directions

Figures presenting the shapes of frontier orbitals, as well as comparison between the measured and simulated absorption and MCD spectra

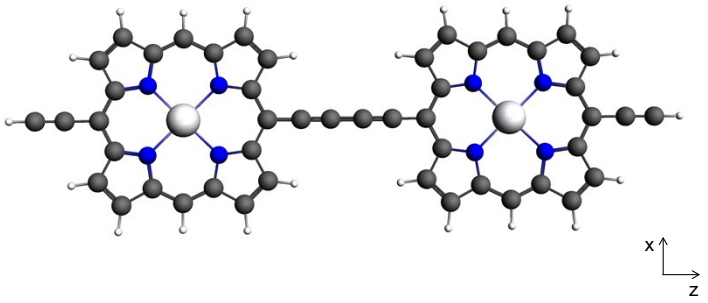
Table S1. Calculated (BP86/TZP) spectral parameters for the molecule used as a model for P1 (see the formula below). Strong transitions indicated by bold font.

	Transition energy [10^3cm^{-1}]	Oscillator strength	*B* term [a]	Polarization
1	**15.74**	**0.2069**	**-12627**	**z**
2	15.80	0.01641	12804	x
3	20.54	3.129E-4	-1.2427	x
4	22.02	0.00227	-6.5134	x
5	**22.28**	**0.8847**	**-2737.4**	**x**
6	22.48	0.00334	15.734	z
7	22.85	1.04E-4	-0.63337	x
8	22.97	0.01448	-123.47	x
9	**23.27**	**1.109**	**2994.5**	**z**
10	23.38	0.00753	11.643	z
11	23.70	9.062E-4	2.7998	y
12	24.25	1.079E-4	-0.45555	x

13	24.58	0.023	183.1	z
14	24.97	0.0061	13.2	z
15	25.29	6.739E-4	-0.18113	mixed [b]
16	25.57	3.133E-4	0.03431	mixed
17	25.70	0.00541	44.016	x
18	25.82	4.932E-4	4.2908	x
19	25.85	3.43E-4	-0.88221	mixed
20	26.05	1.623E-5	0.57299	x

[a] atomic units; [b] since the optimized structure was of low symmetry, mixed polarization was obtained for some weak transitions

Table S2. Calculated (BP86/DZP) spectral parameters for the molecule used as a model for P2 (see the formula below). Strong transitions indicated by bold font. D_{2h} symmetry was assumed.

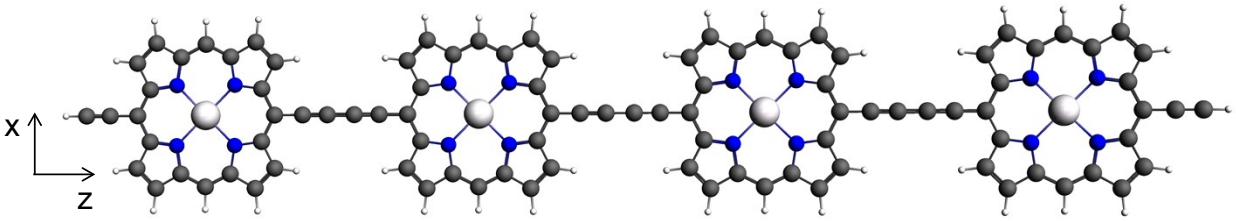


	Transition energy [10^3cm^{-1}]	Oscillator strength	*B* term [a]	Polarization [b]
1B1u	**12.66**	**1.534**	-43.93	**z**
1B3u	14.09	4.19E-4	1.0462	x
2B3u	15.53	0.03258	-556.31	x
2B1u	17.93	6.211E-7	5.042	z
3B1u	17.98	0.02981	-633.36	**z**
3B3u	18.13	0.00165	5152.5	x
4B1u	19.45	0.1076	7.8982	z
4 B3u	20.77	0.00127	1652	x
5 B3u	21.11	3.994E-4	1.8749	**x**
5B1u	**21.39**	**0.8429**	14966	z
6 B3u	**22.23**	**0.1871**	-544.01	**x**
6B1u	**22.27**	**0.3638**	704.5	**z**
1B2u	22.74	8.106E-9	-8.5323	y
2B2u	23.07	1.112E-8	-0.24161	y

7B1u	23.60	0.02264	-29.802	z
7 B3u	**23.81**	**0.4346**	-350.21	**x**
8B1u	24.33	1.449E-6	1.2521	z
8 B3u	24.44	0.03285	-5.022	x
9B1u	24.52	0.06031	-2.7917	z
9B3u	24.69	0.00804	-215.95	x
10B1u	24.71	1.264E-7	-129.04	z
10 B3u	25.00	0.05243	-0.26605	x
3B2u	25.12	5.347E-6	-43.55	y
11B1u	25.63	0.00231	2.5323	z
11 B3u	26.13	0.03585	[b]	x
12B1u	**26.13**	**0.1818**		**z**
13B1u	**26.33**	**0.5427**		**z**
12B3u	**26.96**	**0.1223**		**x**
13B3u	27.21	6.199E-5		x
14B1u	27.27	0.04839		z
B3u	**B3u**	**B3u**		**x**
B3u	**B3u**	**B3u**		**x**
15B3u	28.31	2.361E-5		x
16B3u	**28.47**	**0.1112**		**x**
4B2u	29.16	1.109E-5		y
17B3u	29.31	0.07282		x
16B1u	29.46	1.012E-4		z

[a] atomic units; [b] *B* terms were calculated for the states of lower energy than this one.

Table S3. Calculated (BP86/DZP) spectral parameters for the allowed transitions of the molecule used as a model for P4 (see the formula below). Strong transitions indicated by bold font. D_{2h} symmetry was assumed. Except for lowest 10 allowed transitions, only those with the oscillator strength higher than 0.05 have been included.

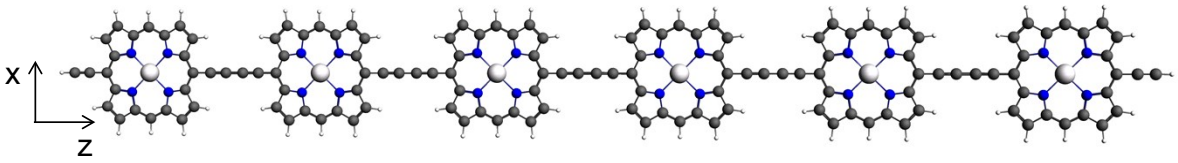


	Transition energy [10^3cm^{-1}]	Oscillator strength	*B* term [a]	Polarization
1B1u	**8.82**	**3.166**	**-71.178**	**z**
2B1u	11.27	0.03177	13.246	z
3B1u	**11.45**	**1.584**	**-72.86**	**z**
1B3u	12.68	1.627E-4	-12.395	x
2B3.u	12.74	0.00148	311.85	x
3B3.u	13.00	0.00457	12.734	x
4B3.u	13.78	0.01022	-197.49	x
4B1.u	**14.39**	**0.142**	**-8775.7**	**x**
5B3.u	14.41	0.00509	-71.178	x
6B3.u	14.65	1.742E-4	13.246	x
6B1u	**15.48**	**0.2092**	**3287.1**	**z**
16B1u	19.42	0.06303	209.16	z
18B1u	**20.22**	**0.1185**	**-39.666**	**z**
19B1u	**20.47**	**1.277**	**-2022.1**	**z**

23B1u	**21.43**	**1.418**	**-63852**	**z**
25B3u	**21.99**	**0.2226**	**-383.11**	**x**
24B1u	22.06	0.06484	1059.4	z
25B1u	**22.37**	**0.1244**	**-217.49**	**z**
27B1u	22.75	0.07774	168.09	z
26B3u	**23.16**	**0.2221**	**44.618**	**x**
28B3u	23.37	0.05057	420.34	x
31B3u	23.70	0.06612	-212.5	x
32B3u	**23.78**	**0.1463**	**232.82**	**x**
33B3u	24.48	0.09106	-149.79	x
42B1u	**24.61**	**0.1227**	**131.47**	**z**
35B3u	24.74	0.08966	234.15	x
37B3u	24.83	0.06005	68.894	x
47B1u	25.26	0.06141	-1031.7	z

[a] atomic units

Table S4. Calculated (BP86/DZP) spectral parameters for the the allowed transitions of the molecule used as a model for P6 (see the formula below). Strong transitions indicated by bold font. Above the lowest 10 allowed transitions, only those with the oscillator strength higher than 0.05 have been included.

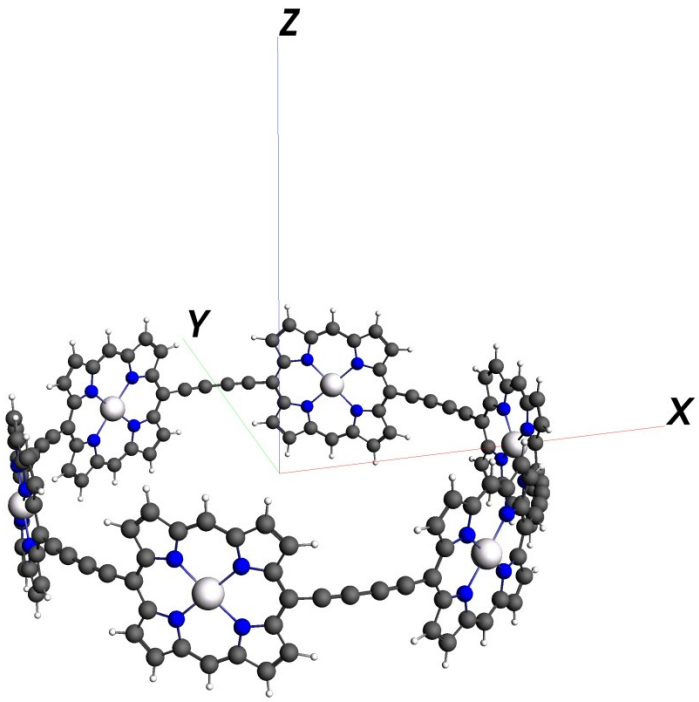


	Transition energy [10^3cm^{-1}]	Oscillator strength	*B* term [a]	Polarization
1B1u	**7.41**	**3.645**	**-90.251**	**z**
2B1u	9.03	0.03395	-2.4078	z
3B1u	**9.14**	**3.224**	**-45.363**	**z**
4B1u	**11.12**	**0.1205**	**13.452**	**z**
5B1u	11.57	0.06109	7.7722	z
6B1u	**11.67**	**1.062**	**-45.448**	**z**
7B1u	11.97	0.0013	4.7506	z
1B3u	12.22	7.581E-4	35.559	**x**
2B3u	12.28	0.00151	241.02	x
3B3u	12.29	2.413E-4	-22.649	x
9B1u	13.88	0.09971	65.536	**z**
11B1u	**14.60**	**0.3154**	**-873.19**	**z**
17B1u	17.51	0.06592	-434.98	**z**
40B1u	**19.91**	**0.4917**	**371.22**	**z**
42B1u	**20.37**	**0.2576**	**-387.28**	**z**
44B1u	**20.55**	**0.7148**	**-852.12**	**z**
45B1u	**20.70**	**1.217**	**-2568.2**	**z**

46B1u	**20.78**	**0.7828**	**-2621.1**	**z**
49B1u	21.18	0.06254	-139.29	z
51B3u	21.49	0.1396	3429.2	**x**
51B1u	21.58	0.1652	79.306	z
52B1u	**21.66**	**0.7085**	**-3937.5**	**z**
54B1u	21.82	0.08872	83.766	**z**
55B3u	**21.92**	**0.19**	**1904.3**	**x**
55B1u	**21.97**	**0.1348**	**258.54**	**z**
56B1u	**22.12**	**0.1124**	**-24.262**	**z**
57B1u	22.41	0.09007	510.34	z
57B3u	22.51	0.08876	-486.06	x
58B3u	22.61	0.07413	33.195	x
63B1u	22.96	0.06583	-382.66	z
65B1u	23.06	0.05403	-28.621	z

[a] atomic units

Table S5. Calculated (BP86/DZP) spectral parameters for the molecule used as a model for c-P6•T6 (see the formula below). Strong transitions indicated by bold font.



	Transition energy [10^3cm^{-1}]	Oscillator strength	*A* term [a]	*B* term [a]	Polarization
1E1u	7.53	6.88E-4	-0.00173	1236.8	xy
2E1u	**10.00**	**5.14**	**19.802**	**54.125**	**xy**
1A2u	11.78	0.00277	0	401.29	z
2A2u	12.35	0.01697	0	-164.63	z
3E1u.	12.75	0.00818	0.05497	-15667	xy
4E1u	**13.36**	**2.326**	**-36.362**	**13560**	**xy**
3A2u	13.85	0.00207	0	1026.3	xy

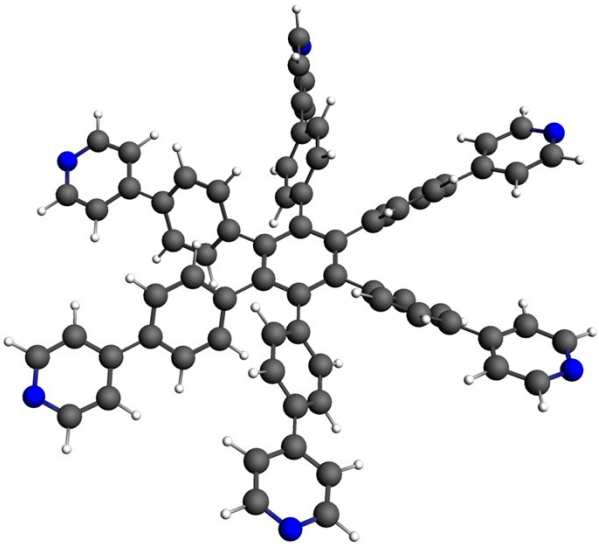
4A2u	**15.04**	**0.18618**	**0**	**-512.65**	**z**
5A2u	16.81	2.329E-6	0	0.42821	z
6A2u	17.04	6.567E-4	0	111.23	z
5E1u	17.76	2.94E-5	-2.678E-7	22.959	xy
6E1u	17.79	0.00321	1.9948E-5	64.252	xy
7E1u	17.83	1.1706E-4	2.4669E-6	-39.018	xy
8E1u	17.88	0.00313	1.9977E-4	31.99	xy
7A2u	18.15	0.09109	0	298.74	xy
13E1u	**19.33**	**0.18364**	**-9.5274**	**-12839**	**xy**
10A2u	19.62	0.04977	0	-774.98	z
14E1u	**19.91**	**0.6758**	**-14.552**	**15487**	**xy**
15E1u	**20.70**	**1.4326**	**8.4513**	**37588**	**xy**
17E1u	**21.11**	**1.3594**	**-30.648**	**14791**	**xy**
18E1u	**21.35**	**0.2034**	**-0.29831**	**-3363.4**	**xy**
19E1u	**21.60**	**0.8128**	**22.322**	**487.97**	**xy**
14A2u	**21.84**	**0.1967**	**0**	**1487.3**	**z**
20E1u	**21.91**	**0.2398**	**-4.7383**	**-15469**	**xy**
15A2u	**21.96**	**0.9674**	**0**	**6259.6**	**z**
21E1u	**22.30**	**0.3436**	**14.155**	**4626.1**	**xy**
16A2u	23.54	0.08262	0	-641.16	z
17A2u	23.75	0.06552	0	310.87	z
19A2u	**23.92**	**0.2486**	**0**	**9790.7**	**z**
31E1u	**23.93**	**0.12442**	**-4.3447**	**-9031**	**xy**

[a] atomic units

Table S6. Calculated (BP86/DZP) spectral parameters for T6. Strong transitions indicated by bold font. The optimized structure is shown below.

	Transition energy [$10^3 cm^{-1}$]	Oscillator strength	*B* term [a]
1	23.73	0.00233	-4.5119
2	**24.70**	**0.2638**	**-6043.9**
3	**24.75**	**0.1533**	**-564.67**
4	**24.76**	**0.2172**	**6286.5**
5	24.85	0.0106	158.16
6	24.88	0.00846	78.894
7	25.17	0.00347	-4.5263
8	25.21	0.00242	-2.6278
9	25.36	5.79E-4	3.5672
10	25.39	0.00146	-0.02323
11	28.58	0.09174	121.57
12	28.72	0.06403	-197.85

[a] atomic units



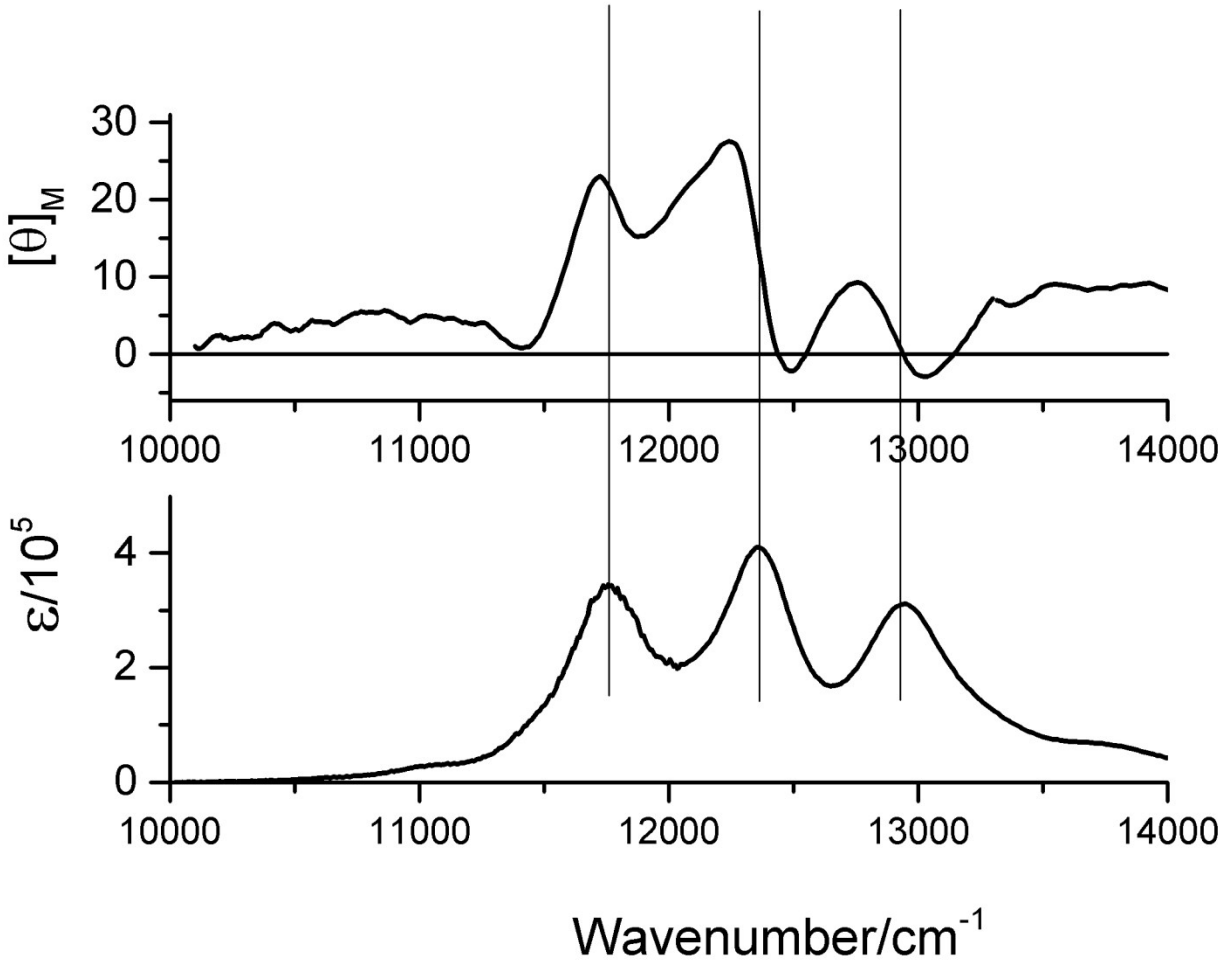


Figure S1. Absorption and MCD spectra of ***c*-P6•T6** in the low energy region. The vertical lines are inserted to show that the maxima on both curves do not coincide.

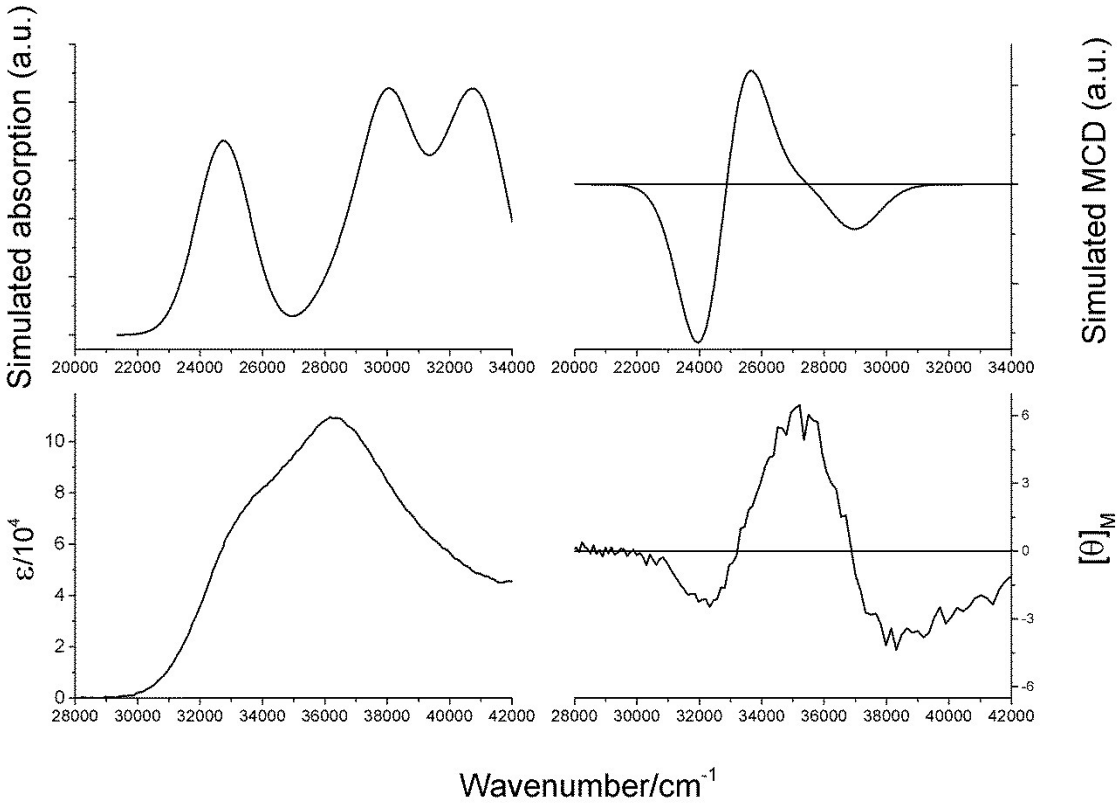


Figure S2. Bottom, experimental, top, simulated absorption and MCD spectra of **T6**. 2000 cm^{-1} bandwidth was assumed in the simulations.

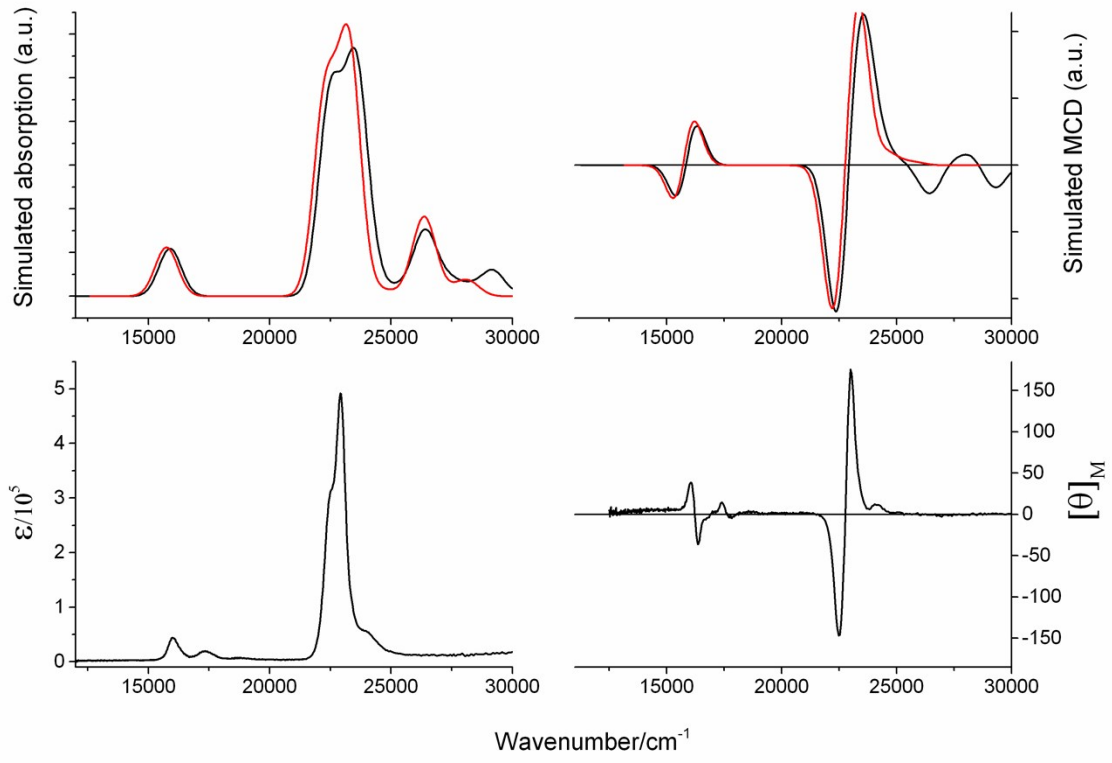


Figure S3. Experimental (bottom) and calculated (top) absorption and MCD spectra of **P1**. Red, BP86/TZP, black, SAOP/TZP. 2000 cm^{-1} bandwidth was assumed in the simulations.

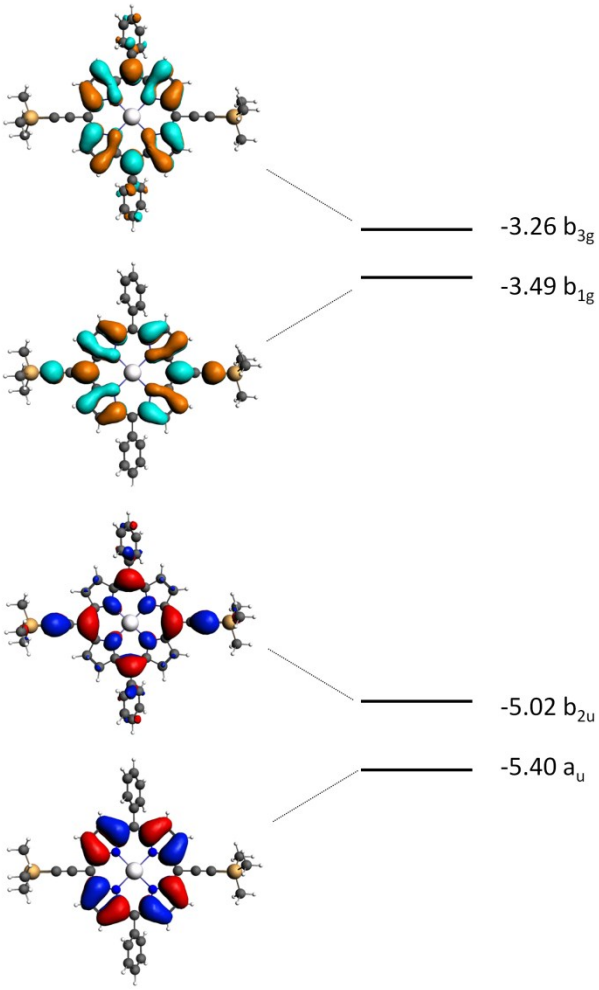


Figure S4. Frontier molecular orbitals of P1 (TZP/BP86). The symmetry species refer to the idealized D_{2h} symmetry.

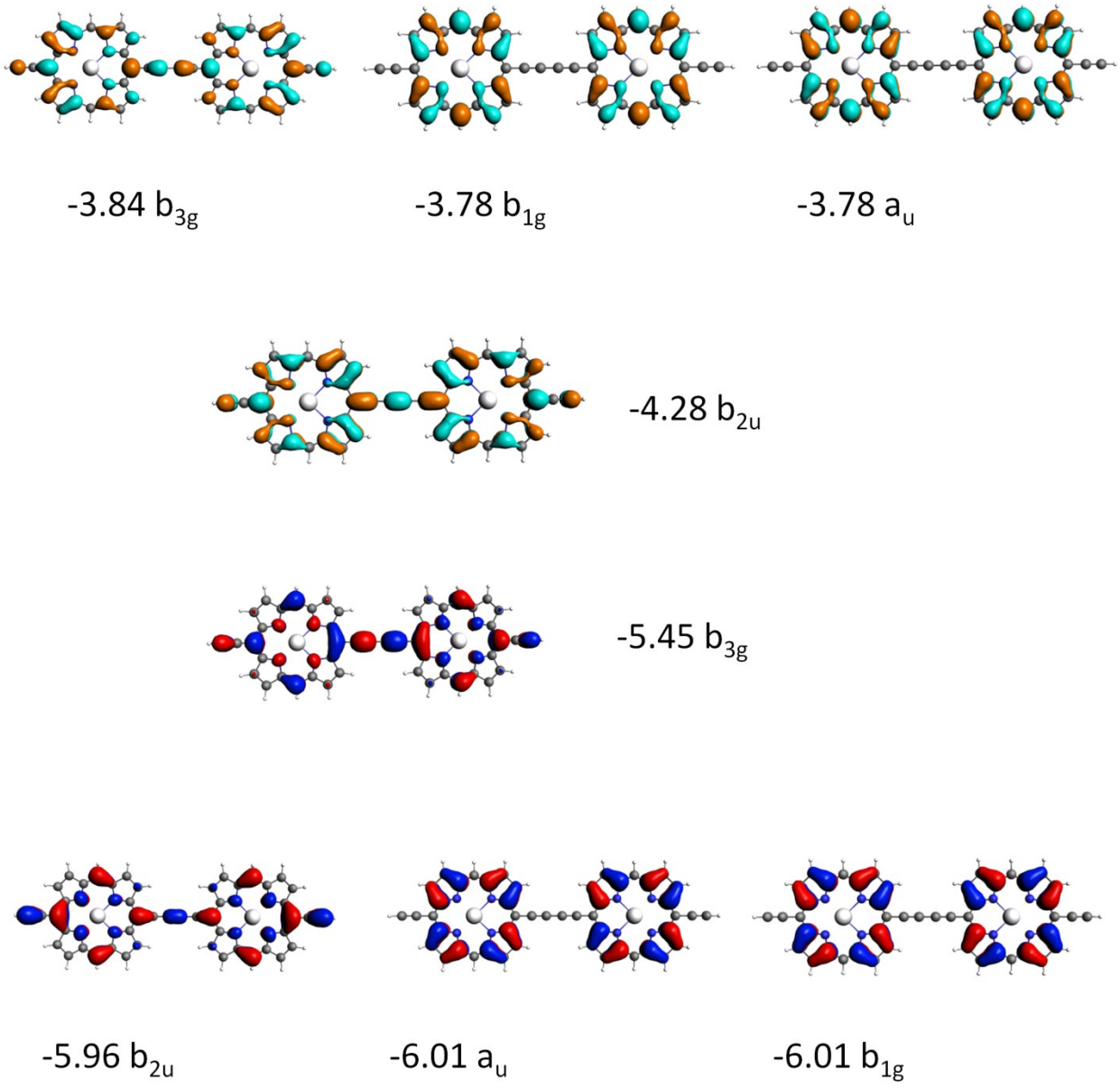


Figure S5. Frontier molecular orbitals of the planar, D_{2h} symmetry form of P2 (DZP/BP86).

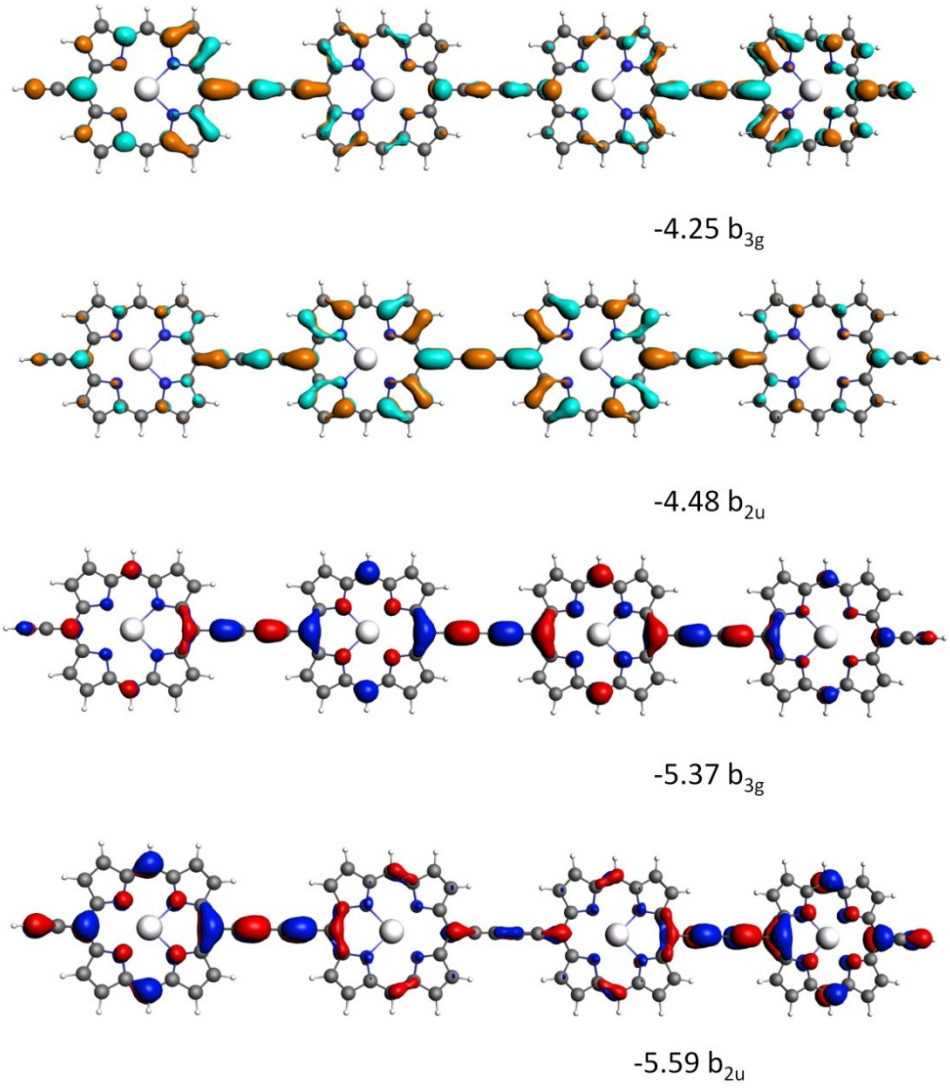


Figure S6. Frontier molecular orbitals of the planar, D_{2h} symmetry form of P4 (DZP/BP86).

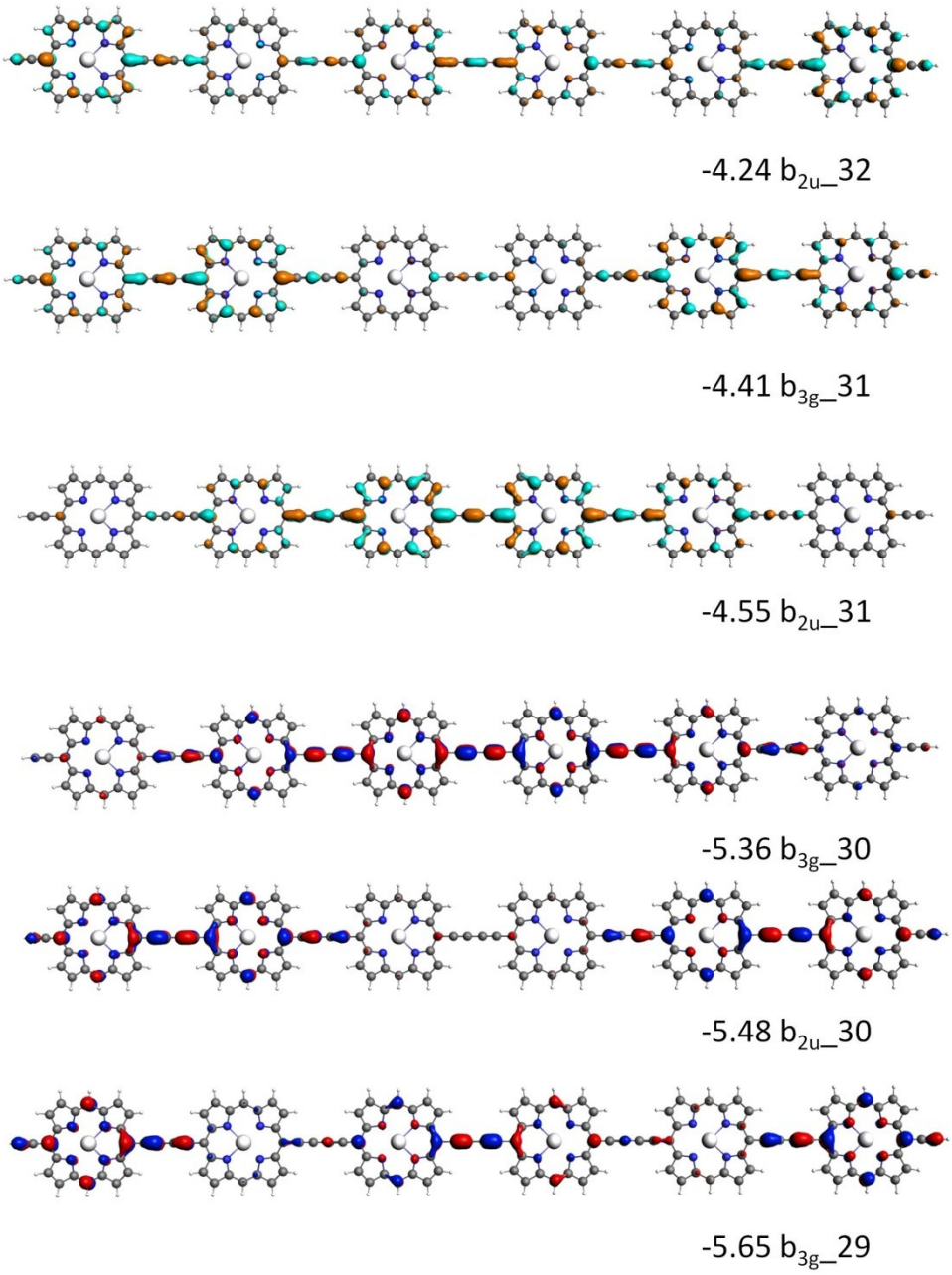


Figure S7. Frontier molecular orbitals of the planar, D_{2h} symmetry form of P6 (DZP/BP86).

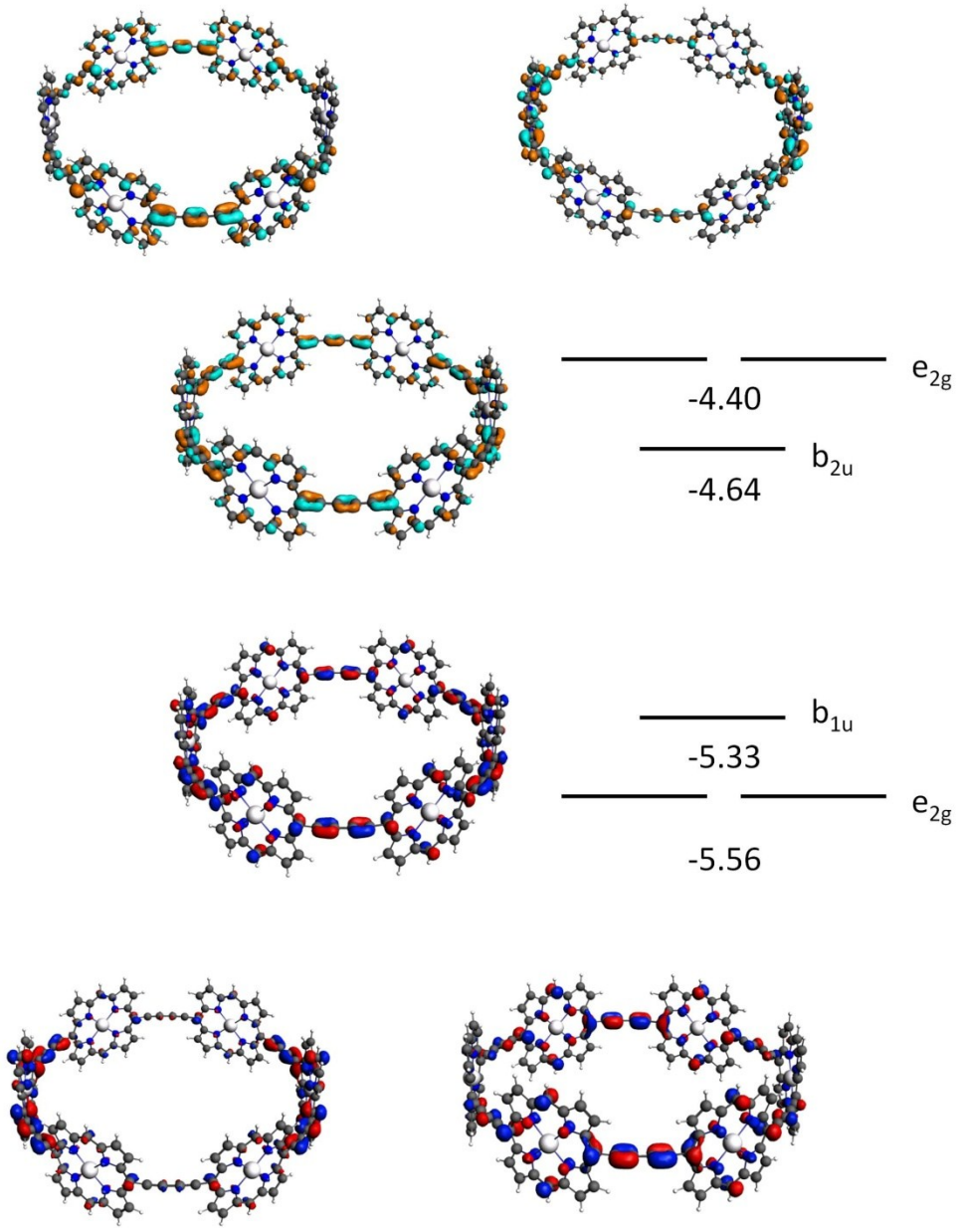


Figure S8. Frontier molecular orbitals of c-P6 (D_{6h} symmetry, DZP/BP86).

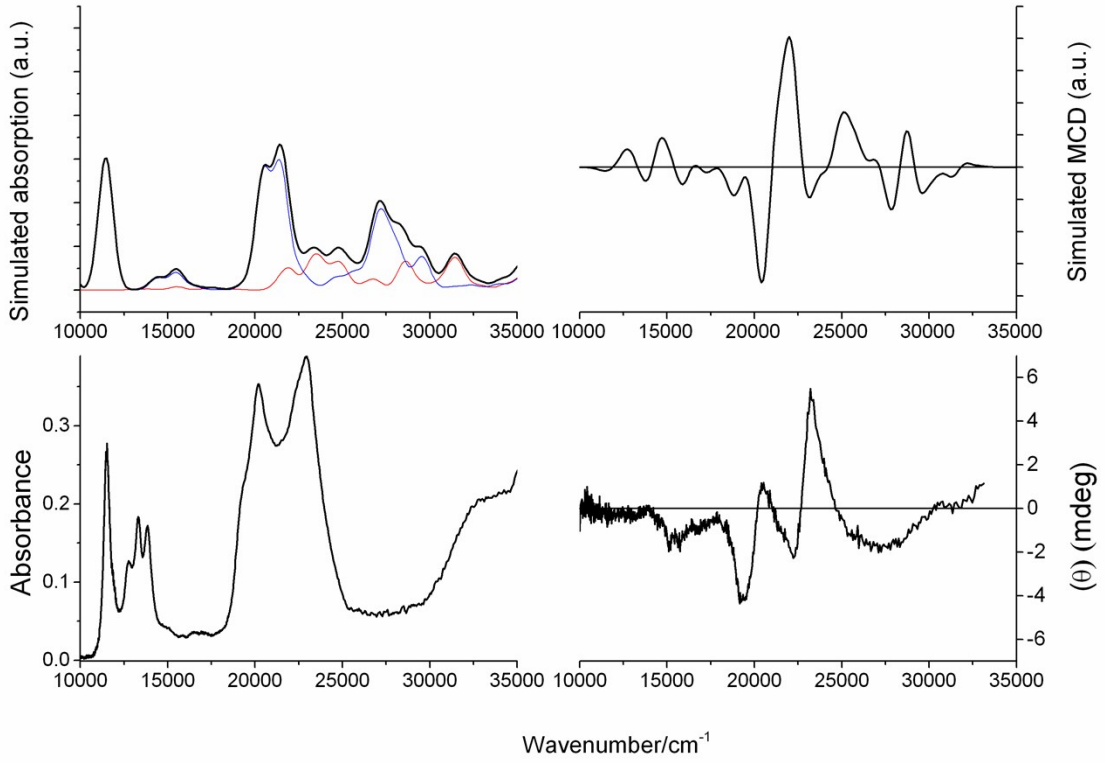


Figure S9. Experimental (bottom) and calculated (top) absorption and MCD spectra of P4. The simulated absorption spectrum (black) consists of long- and short-axis polarized components (blue and red, respectively). 1000 cm^{-1} bandwidth was assumed in the simulations.The experimental spectra are those obtained for P4 complexed with T6.

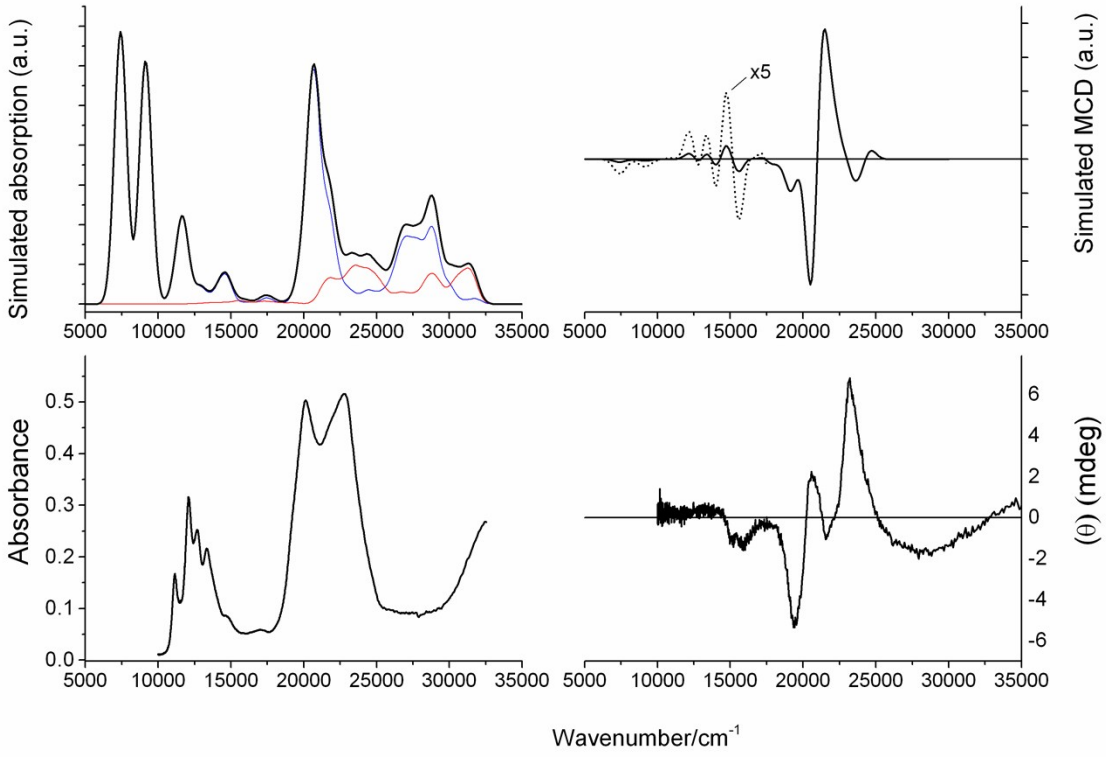


Figure S10. Experimental (bottom) and calculated (top) absorption and MCD spectra of P6. The simulated absorption spectrum (black) consists of long- and short-axis polarized components (blue and red, respectively). 1000 cm^{-1} bandwidth was assumed in the simulations. The experimental spectra are those obtained for P6 complexed with T6.