Detailed Assignment of the Magnetic Circular Dichroism and UV-Vis Spectra of Five-Coordinate High-Spin Ferric [Fe(TPP)(Cl)]

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Supporting Information

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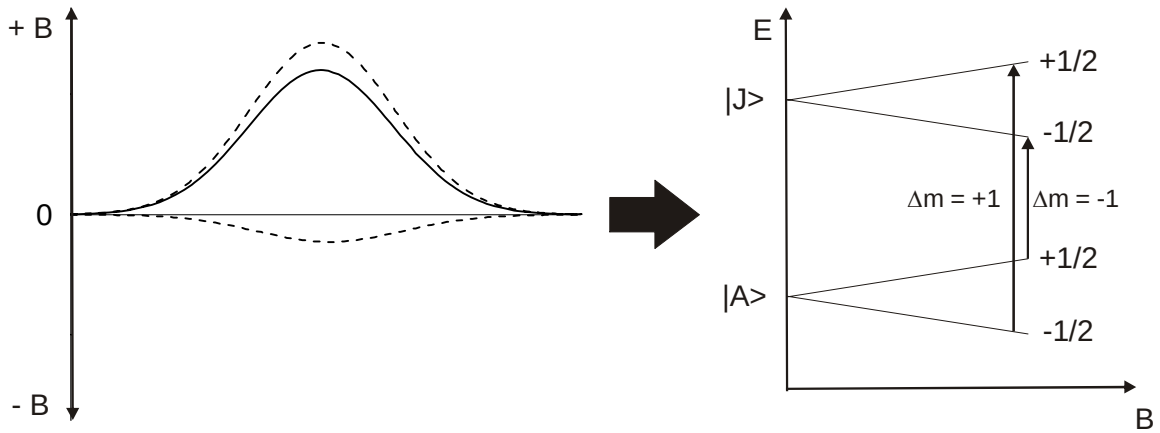
S.1 MCD Theory

Scheme S1.



S.2 Method calibration for quantum-chemical excited state calculations using four-coordinate zinc porphyrins: [Zn(P)] and [Zn(TPP)].

In order to assign the UV-Vis absorption and MCD spectra of [Fe(TPP)(Cl)], quantum-chemical excited state calculations were performed. To explore the performance of TD-DFT and semiempirical INDO/S-CI calculations on metalloporphyrins, we have calculated the absorption spectra of the simple [Zn(P)] (P^{2-} = porphine) and [Zn(TPP)] (TPP^{2-} = tetraphenylporphyrin) complexes first, and compared the results to the experimental data of [Zn(TPP)][1], which show a very simple absorption spectrum. The results are summarized in Table S1 in the Supporting Information. $Zinc^{2+}$ is a good choice for these method calibration studies, because it has a d^{10} electron configuration and therefore, no charge transfer (CT) transitions from the porphyrin to the metal are possible, and no d-d transitions are present. Correspondingly, [Zn(TPP)] shows a very simple absorption spectrum, which allows for the straight-forward identification of the Soret and Q bands at 23880 and 17080 cm^{-1}, respectively. The Soret and Q transitions are also easy to identify in the calculations. As shown in Table S1, the calculations clearly

indicate that the simple porphine ligand is not a good model for TPP in both the TD-DFT and INDO/S-CI calculations producing significant errors in comparison with the experimental data for [Zn(TPP)]. This is not surprising, because the phenyl substituents have a critical influence on the geometric and electronic structure of the porphyrin core. These effects cannot be neglected if the calculation of porphyrin $\pi \rightarrow \pi^*$ transitions is desired. Hence, the complete TPP ligand has to be used in the theoretical treatment. The TD-DFT calculations on simple [Zn(P)] also show that more accurate results are obtained by adding polarization functions (from TZVP) to the LanL2DZ basis set on all heavy atoms (LanL2DZ* basis set)[2]. A further extension of the basis set to TZVP does not lead to a noticeable improvement, which indicates that LanL2DZ* is sufficient for the TD-DFT calculations (cf. Table S1). However, there are still considerable deviations to experiment, and therefore, the TD-DFT results by themselves are not sufficient for a quantitative interpretation of the complicated electronic spectra of high-spin (hs) ferric hemes. This requires further experimental input. Nevertheless, the calculations can be used to define the "active space" of electronic transitions, which need to be considered for the analysis, and their relative energies. This is very useful for the assignment of the spectra.

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[1] Gouterman, M. in *The Porphyrins*; Dolphin, D., Ed.; Academic: New York, 1979, Vol. III, Part A, pp 1-156.
[2] Praneeth, V. K. K.; Näther, C.; Peters, G.; Lehnert, N. *Inorg. Chem.* **2005**, *45*, 2795-2811.

S.3 Complete ref.[16]

Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A.; Vreven, Jr., T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.;

Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A., Gaussian 03, Gaussian, Inc., Pittsburgh PA, 2003.

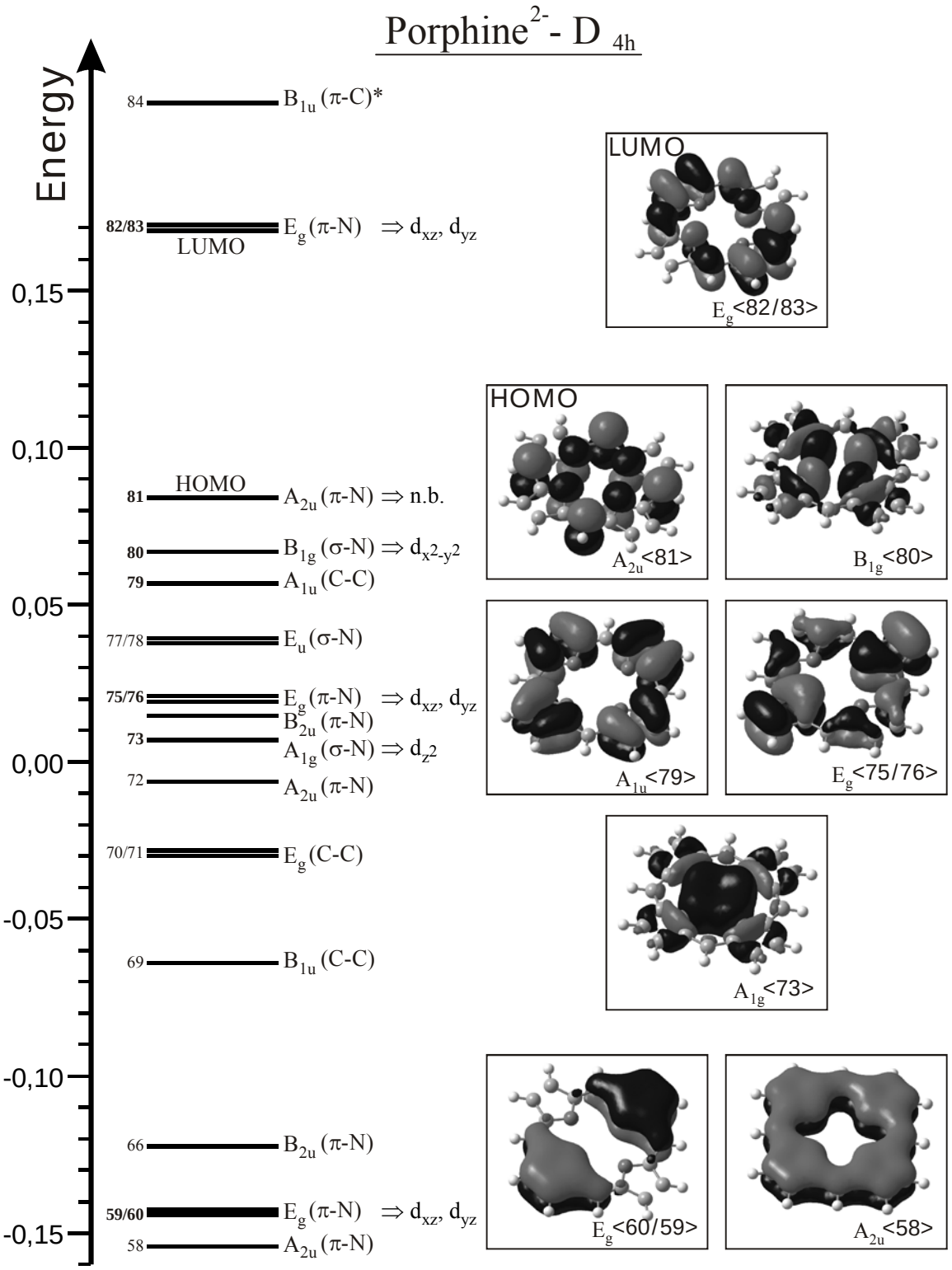

Figure S1. MO diagram of the free porphine(2-) ligand and contour plots. Energies are given in Hartree. Metal d orbitals that potentially interact with these MOs are indicated (labels are based on the coordinate system given in Figure 1).

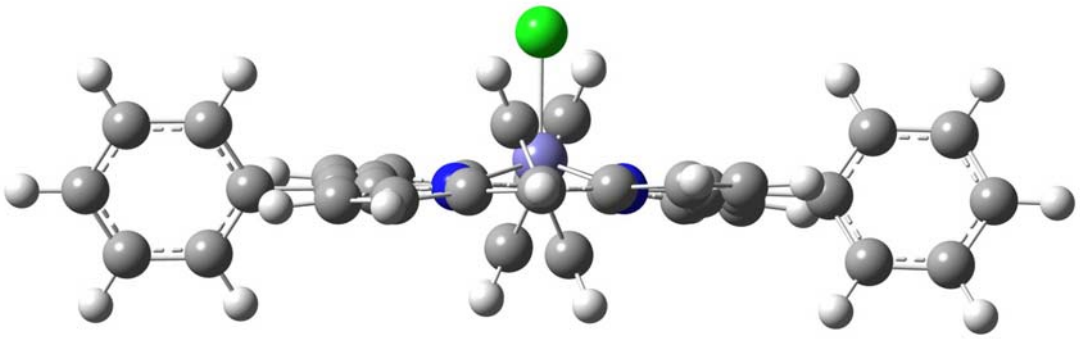

Figure S2. Side view of the optimized (B3LYP/LanL2DZ*) structure of [Fe(TPP)(Cl)] with d(Fe-Cl) = 2.192 Å (taken from crystal structure; see: Hoard, J. L.; Cohen, G. H.; Glick, M. D. *J. Am. Chem. Soc.* **1967**, *89*, 1992-1996.).

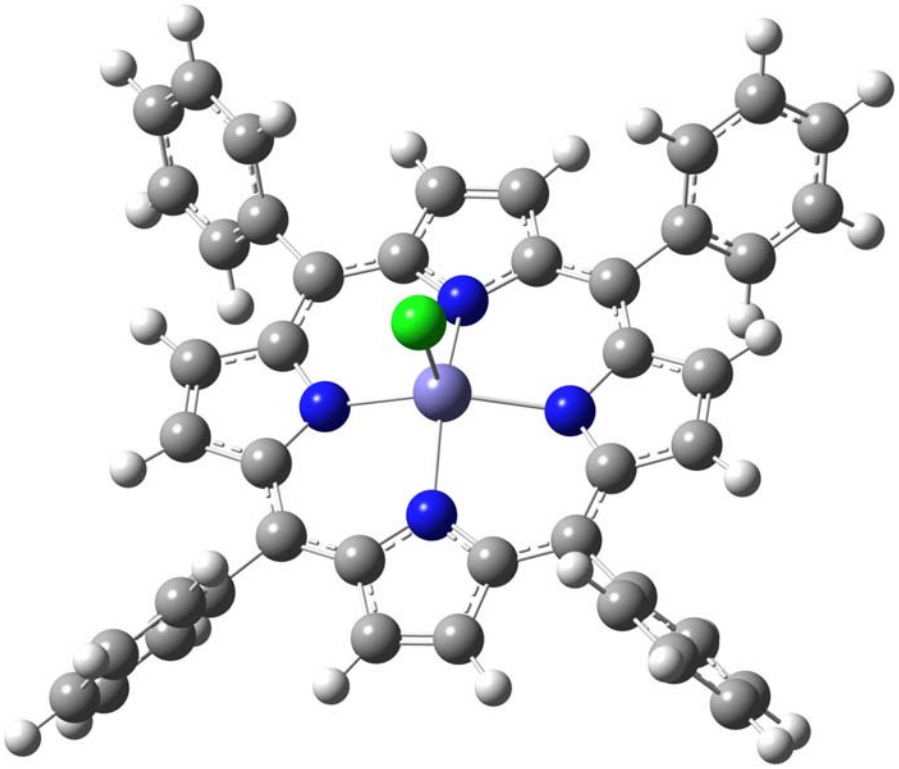

Figure S3. Top view of the optimized (B3LYP/LanL2DZ*) structure of [Fe(TPP)(Cl)] with d(Fe-Cl) = 2.192 Å (taken from crystal structure; see: Hoard, J. L.; Cohen, G. H.; Glick, M. D. *J. Am. Chem. Soc.* **1967**, *89*, 1992-1996.).

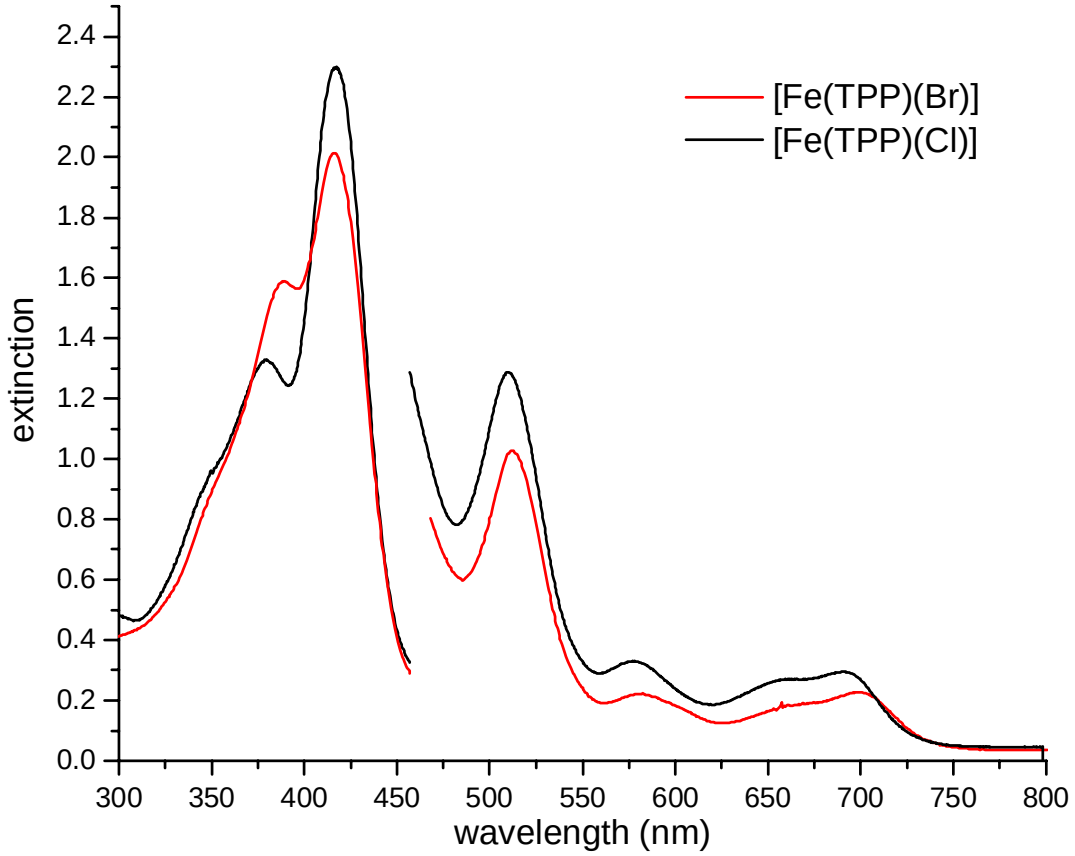

Figure S4. UV-Vis absorption spectra of [Fe(TPP)(X)] (X= Cl and Br)

Table S1. TD-DFT and INDO/S calculations on [Zn(P)] and [Zn(TPP)].

Assignment	[Zn(P)]				[Zn(TPP)]		Exp.[a]
	B3LYP LanL2DZ	B3LYP LanL2DZ*	B3LYP TZVP	INDO/S-CI	B3LYP LanL2DZ	INDO/S-CI	
Soret	28190	27700	27620	26952	26810	25008	23880
Q	19281	18940	18980	14546	18660	14250	17080

[a] Gouterman, M. in *The Porphyrins*; Dolphin, D., Ed.; Academic: New York, 1979, Vol. III, Part A, pp 1-156.

Table S2. TD-DFT (B3LYP/LanL2DZ*) results (Contributions are given in %).

No.	1	2	3	4	5	6
Excitation energy, cm^{-1} (nm, f)	8342 (1199, 0.0010)	8800 (1136, 0.0009)	11945 (837, 0.0023)	12325 (811, 0.0004)	12329 (811, 0.0029)	12910 (775, 0.0026)
Inner Porphyrin Excitations:						
$\pi \rightarrow \pi^{*(0)}$	4	6	-	-	27	45
$\pi \rightarrow \pi^{*(1)}$	-	-	-	-	-	-
$\pi \rightarrow \pi^{*(2)}$	-	-	-	-	-	-
Porphyrin to Fe Excitations:						
$CT^{(1)}$	-	-	-	-	**73**	55
$CT^{(2)}$	**88**	**86**	-	-	-	-
$CT^{(3)}$	-	-	-	-	-	-
$CT^{(4)}$	3	3	-	-	-	-
$CT^{(5)}$, z	-	-	**82**	10	-	-
Chloro to Fe Excitations:						
$CT^{(Cl,1)}$, z	-	-	2	-	-	-
$CT^{(Cl,2)}$, z	-	-	2	-	-	-
$CT^{(Cl,3)}$, z	-	-	1	-	-	-
Other contributions				A_{1u} <168> → d_{xy}: **90**		

Table S2. TD-DFT (B3LYP/LanL2DZ*) results (continued).

No.	7	8	9	10	11	12
Excitation energy, cm^{-1} (nm, f)	16783 (596, 0.0072)	16921 (591, 0.0053)	18988 (527, 0.0214)	18990 (527, 0.0146)	20740 (482, 0.0011)	21025/21115 (476/474, 0.0089/0.0071)
	$Q^{\alpha\ a}$	$Q^{\alpha\ a}$	$Q^{\beta\ a}$	$Q^{\beta\ a}$		
Inner Porphyrin Excitations:						
$\pi \rightarrow \pi^{*(0)}$	**96**	**97**	**97**	**98**	-	8
$\pi \rightarrow \pi^{*(1)}$	-	-	-	-	-	-
$\pi \rightarrow \pi^{*(2)}$	-	-	-	-	-	-
Porphyrin to Fe Excitations:						
$CT^{(1)}$	4	3	-	-	-	-
$CT^{(2)}$	-	-	3	2	-	-
$CT^{(3)}$	-	-	-	-	-	-
$CT^{(4)}$	-	-	-	-	-	-
$CT^{(5)}$, z	-	-	-	-	-	-
Chloro to Fe Excitations:						
$CT^{(Cl,1)}$, z	-	-	-	-	3	-
$CT^{(Cl,2)}$, z	-	-	-	-	4	-
$CT^{(Cl,3)}$, z	-	-	-	-	-	-
Other contributions					$E_g \rightarrow d_\pi$: **92**	$E_g \rightarrow d_{z2}$: **82**

[a] Two sets of Q bands are predicted (four bands) due to spin polarization. Bands 7 and 8 have more α-spin $\pi \rightarrow \pi^{*(0),\alpha}$, whereas bands 9 and 10 have more β-spin $\pi \rightarrow \pi^{*(0),\beta}$ character.

Table S2. TD-DFT (B3LYP/LanL2DZ*) results (continued).

No.	13	14	15	16	17	18
Excitation energy, cm^{-1} (nm, f)	21631 (462, 0.0118)	22341 (448, 0.0219)	22455 (445, 0.0134)	22605 (442, 0.0007)	24410 (410, 0.1310)	24446 (409, 0.1364)
Inner Porphyrin Excitations:						
$\pi \rightarrow \pi^{*(0)}$	5	6	-	-	21	21
$\pi \rightarrow \pi^{*(1)}$	-	-	-	-	-	-
$\pi \rightarrow \pi^{*(2)}$	2	2	-	-	5	6
Porphyrin to Fe Excitations:						
$CT^{(1)}$	-	-	-	-	-	-
$CT^{(2)}$	-	-	-	-	-	-
$CT^{(3)}$	**89**	**89**	-	-	-	-
$CT^{(4)}$	-	-	-	-	10	8
$CT^{(5)}$, z	-	-	-	-	-	-
$CT^{(6)}$, z	-		6	**90**		
Chloro to Fe Excitations:						
$CT^{(Cl,1)}$, z	-	-	-	-	-	-
$CT^{(Cl,2)}$, z	-	-	-	-	-	-
$CT^{(Cl,3)}$, z	-	-	4	-	-	-
Other contributions			$E_g \rightarrow d_\pi$: **88**		$p_{x,y} \rightarrow d_{z2}$: **52**	$p_{x,y} \rightarrow d_{z2}$ **53 %**

Table S2. TD-DFT (B3LYP/LanL2DZ*) results (continued).

No.	19	20	21	22	23	24
Excitation energy, cm^{-1} (nm, f)	25008 (400, 0.0009)	25202 (397, 0.0323)	25203 (397, 0.0041)	25475 (393, 0.0024)	25718 (389, 0.0333)	25843 (387, 0.1016)
						Soret?
Inner Porphyrin Excitations:						
$\pi \rightarrow \pi^{*(0)}$	-	2	-	-	-	6
$\pi \rightarrow \pi^{*(1)}$	-	-	6	2	-	31
$\pi \rightarrow \pi^{*(2)}$	-	6	-	**41**	24	
Porphyrin to Fe Excitations:						
$CT^{(1)}$	-	-	-	-	-	
$CT^{(2)}$	-	3	-	20	5	4
$CT^{(3)}$	-	-	-	2	1	2
$CT^{(4)}$	-	**49**	-	-	-	
$CT^{(5)}$, z	28	-	-	-	-	
$CT^{(Cl,1)}$, z	**38**	-	1	-	-	
$CT^{(Cl,2)}$, z	1	-	6	-	-	
$CT^{(Cl,3)}$, z	13	-	-	-	-	
Other contributions			$A_{2u} \rightarrow B_{1u}$: **35**		Ph $\rightarrow d_{xy}$: **54**	Ph $\rightarrow d_{xy}$: **41**

Table S2. TD-DFT (B3LYP/LanL2DZ*) results (continued).

No.	25	26	27	28	29	
Excitation energy, cm^{-1} (nm, f)	26071 (384, 0.3805)	26109 (383, 0.1539)	26143 (383, 0.5366)	27164 (368, 0.0967)	27250 (367, 0.0098)	
	Soret?	Soret?	Soret?			
Inner Porphyrin Excitations:						
$\pi \rightarrow \pi^{*(0)}$	14	11	23	1	-	
$\pi \rightarrow \pi^{*(1)}$	-	1	3	2	2	
$\pi \rightarrow \pi^{*(2)}$	20	23	24	**83**	**77**	
Porphyrin to Fe Excitations:						
$CT^{(1)}$	-	-	2	-	-	
$CT^{(2)}$	2	-	-	2	-	
$CT^{(3)}$	2	4	2	-	-	
$CT^{(4)}$	11	34	-	-	-	
$CT^{(5)}$, z	-	-	-	-	-	
Chloro to Fe Excitations:						
$CT^{(Cl,1)}$, z	-	-	-	-	-	
$CT^{(Cl,2)}$, z	-	-	-	-	-	
$CT^{(Cl,3)}$, z	-	-	-	-	-	
Other contributions	Ph $\rightarrow d_{\pi,z2}$: 19	Ph $\rightarrow d_{\pi,z2}$: 11	Ph $\rightarrow d_{\pi,z2}$: 16			

Table S3. Optimized (B3LYP/LanL2DZ*) structure of [Fe(TPP)(Cl)] with d(Fe-Cl) set to 2.192 Å. Coordinates are given in Å

Atom type	x	Y	z
C	4.26625300	0.46927500	-0.34561900
C	4.19585000	-0.89774300	-0.36234900
C	2.91436200	0.95902400	-0.18383000
H	5.14690000	1.09118800	-0.45766400
C	2.80108400	-1.25003500	-0.20620900
N	2.03456500	-0.10400400	-0.11587200
C	2.57356400	2.32428100	-0.13266700
H	5.00838600	-1.60357700	-0.49019400
C	1.25124900	2.80423200	-0.09720600
C	2.32238200	-2.57346400	-0.17321500
C	3.69076400	3.32436000	-0.12305800
C	0.89893500	4.20536800	-0.01869300
N	0.10473600	2.03205100	-0.13986700
C	0.95836500	-2.91623800	-0.11908300
C	3.32804300	-3.68532900	-0.20600900
C	3.91412600	4.17212300	-1.22583400
C	4.54224200	3.42931500	0.99451600
C	-0.46796200	4.27465800	-0.03424400
C	-0.95834900	2.91616400	-0.11965400
C	0.46788600	-4.27475400	-0.03425800
N	-0.10466900	-2.03208300	-0.13933400
H	1.60465100	5.02475200	0.05404600
C	3.43566500	-4.52572300	-1.33159600
C	4.18530600	-3.90863500	0.88950500
C	4.96629700	5.10036300	-1.21377900
C	5.58854600	4.36374900	1.01220200
H	3.26868300	4.09250600	-2.10111200
H	4.37289900	2.78395300	1.85689500
C	-2.32236400	2.57338700	-0.17380500
C	-1.25121400	-2.80422100	-0.09699700
C	-0.89899700	-4.20535200	-0.01807500
H	-1.08920000	5.16088800	0.02416200
H	1.08906900	-5.16103500	0.02389900
C	4.38062300	-5.56229400	-1.36401100
C	5.12408900	-4.95104000	0.86272800
H	2.78375400	-4.35667900	-2.18916300
H	4.10364500	-3.27097100	1.77022100
C	5.80641200	5.20143800	-0.09334900
H	5.12994400	5.74222600	-2.08005300
H	6.23166000	4.43708200	1.88975900
C	-2.80109900	1.24997800	-0.20660500
C	-2.57349800	-2.32427700	-0.13271700
C	-3.32798500	3.68530500	-0.20646100
H	-1.60480100	-5.02466900	0.05465200
C	5.22709100	-5.78071400	-0.26528100
H	4.45544200	-6.19742800	-2.24730900
H	5.77263000	-5.11512900	1.72385400
H	6.62215200	5.92501500	-0.08210200
C	-4.19596500	0.89766000	-0.36187300
C	-2.91434200	-0.95906600	-0.18400300

C	-3.69066000	-3.32444100	-0.12310200
N	-2.03451400	0.10396700	-0.11656000
C	-4.18429500	3.90940000	0.88963200
C	-3.43652400	4.52491400	-1.33254000
H	5.95881800	-6.58891800	-0.28772900
C	-4.26629400	-0.46936500	-0.34541300
H	-5.00859000	1.60349100	-0.48916100
C	-3.91660700	-4.16915200	-1.22767700
C	-4.53948900	-3.43240700	0.99617800
C	-5.12305100	4.95183400	0.86293600
C	-4.38145700	5.56151300	-1.36486300
H	-4.10192800	3.27232200	1.77070600
H	-2.78533700	4.35525100	-2.19053500
H	-5.14696600	-1.09133200	-0.45699000
C	-4.96873400	-5.09745300	-1.21567100
C	-5.58573900	-4.36691600	1.01378400
C	-5.22697300	5.78073400	-0.26555900
H	-3.27316200	-4.08717700	-2.10421000
H	-4.36818000	-2.78930500	1.85985900
H	-5.77085700	5.11654700	1.72449700
H	-4.45699700	6.19604600	-2.24853000
C	-5.80618600	-5.20159800	-0.09352900
H	-5.13441200	-5.73697500	-2.08328800
H	-6.22681200	-4.44263300	1.89263000
H	-5.95868200	6.58895600	-0.28794200
H	-6.62188900	-5.92521700	-0.08232800
Fe	-0.00006400	0.00007800	0.35440800
Cl	-0.00046340	0.00035138	2.54640795