Density Functional Theory Based Configuration Interaction Calculations on the Electronic Spectra of Free-Base Porphyrin, Chlorin, Bacteriochlorin, and *cis*- and *trans*-Isobacteriochlorin

Andreas B. J. Parusel*,† and Abhik Ghosh*,‡

NASA Ames Research Center, MS 239-4, Moffett Field, California 94035, and Institute of Chemistry, Faculty of Science, University of Tromsø, 9037 Tromsø, Norway

Received: June 23, 1999; In Final Form: November 29, 1999

Configuration interaction calculations with single excitations based on density functional theory (DFT/SCI) provide a reasonably accurate description of the electronic spectra of prototype porphyrin-type molecules at modest computational cost. The calculations reproduce the experimentally observed Q−B energy splitting, differences in Q and B oscillator strengths, and the intensification, relative to porphyrin, of Q_x bands of hydroporphyrins. In all cases, the DFT/SCI results are in comparable or better agreement with experiment, compared to recent *ab initio* CASPT2, SAC−CI, and STEOM-CCSD calculations.

I. Introduction

In recent years, first-principles quantum chemical calculations have illuminated diverse aspects of porphyrins and related molecules, such as molecular structures and conformation, photoelectron spectra and redox potentials, and ground-state electron distributions.[1,2] However, accurate calculations of the excited states of tetrapyrroles remain a difficult problem. The electronic spectra of some of the more simple tetrapyrroles have been studied with multiconfigurational second-order perturbation theory (CASPT2),[3] symmetry-adapted cluster configuration interaction (SAC−CI),[4−6] and similarity-transformed equation-of-motion coupled cluster theory (STEOM-CCSD).[7,8] However, these methods do not provide a sufficiently general solution to calculations of the excited states of porphyrin-type molecules with low symmetry and complex substitution patterns. The CASPT2 method is computationally demanding, and significant discrepancies have been observed between theory and experiment for all these methods.[3−8] We were therefore intrigued by the possible use of density functional theory (DFT),[9] already extremely successful in many problems involving porphyrins, for simulating the electronic spectra of porphyrin-type molecules. Here we illustrate the performance of density functional theory based configuration interaction singles calculations (DFT/SCI)[10] on prototype free-base tetrapyrroles (Figure 1), viz., porphyrin (PH_2, D_{2h}), chlorin (CH_2, C_{2v}), bacteriochlorin (BH_2, D_{2h}), and the *cis* (C_{2v}) and *trans* (C_s) tautomers of isobacteriochlorin (IH_2). The results compare well with experiment, proving the great potential of DFT-based investigations of the rich optical properties, photochemistry, and photobiology of porphyrin-type molecules.

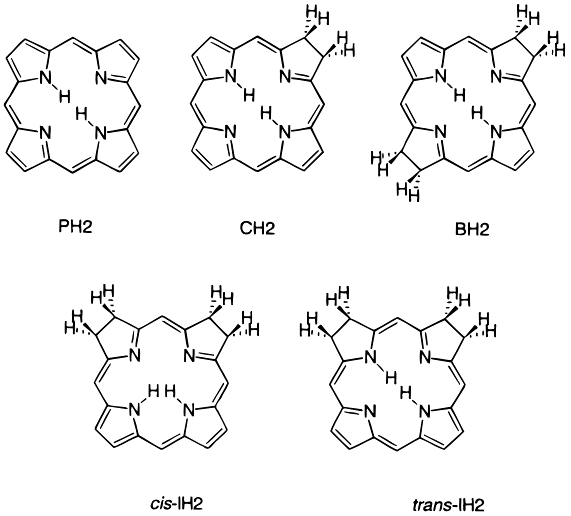

Figure 1. Molecules studied in this work.

II. Computational Methods

All molecular geometries were optimized at the nonlocal DFT/TZP level and taken from our previous work.[1,2] All excited-state calculations have been performed using the DFT/SCI method described by Grimme.[10] The method is based on the single-excitation configuration interaction (SCI) approach with the CI Hamiltionian matrix elements modified and corrected empirically. Molecular orbital eigenvalues are taken from gradient-corrected Kohn−Sham DFT for the construction of the CI Hamiltonian matrix.[10] The calculations have been performed with the TURBOMOLE suite of programs,[11,12] valence double-ζ Gaussian basis sets with d-polarization functions for carbon and nitrogen (C, N [3s2p1d], H [2s]) (VDZP),[13] and Becke's hybrid exchange-correlation functional (B3LYP).[14,15] We also tested a smaller basis set VDZ[13] in which all polarization functions from the VDZP set have been discarded (C, N [3s2p], H [2s]). We also tested a valence triple-ζ basis set with polarization functions (VTZP)[16] for PH_2 (C, N [5s3p1d], H [3s]). All single excitations from the occupied valence MOs to the virtual space were included in the DFT/SCI calculations. The D_{2h} symmetry labels refer to an orientation of the porphyrin molecule in which the two protonated nitrogen atoms lie along the x axis and the two unprotonated nitrogen atoms lie along the y axis.

[†] NASA Ames Research Center. Fax: (650) 604-1088. E-mail: parusel@camelot.arc.nasa.gov.

[‡] University of Tromsø. Fax: +47 77644765. E-mail: abhik@chem.uit.no.

10.1021/jp9921046 CCC: $19.00

TABLE 1: Orbital Energies (eV) and Symmetries of Some Frontier Orbitals of PH_2

	VDZ		VDZP		VTZP	
LUMO + 7	b_{3u}	1.99	a_u	1.98	b_{3g}	1.36
LUMO + 6	b_{3g}	1.71	a_g	1.71	b_{3u}	1.35
LUMO + 5	a_g	1.71	b_{3g}	1.67	b_{2g}	1.35
LUMO + 4	b_{2g}	1.63	b_{2g}	1.61	a_g	1.11
LUMO + 3	b_{1u}	1.25	b_{1u}	1.22	b_{1u}	1.04
LUMO + 2	a_u	−0.82	a_u	−0.80	a_u	−0.91
LUMO + 1	b_{3g}	−2.39	b_{2g}	−2.37	b_{2g}	−2.49
LUMO	b_{2g}	−2.41	b_{3g}	−2.39	b_{3g}	−2.50
HOMO	b_{1u}	−5.25	b_{1u}	−5.25	b_{1u}	−5.37
HOMO − 1	a_u	−5.63	a_u	−5.52	a_u	−5.61
HOMO − 2	b_{3g}	−6.51	b_{3g}	−6.44	b_{3g}	−6.55
HOMO − 3	b_{1u}	−6.65	b_{1u}	−6.58	b_{1u}	−6.68
HOMO − 4	a_g	−7.18	a_g	−7.31	b_{2g}	−7.41
HOMO − 5	b_{2u}	−7.21	b_{2g}	−7.32	b_{1u}	−7.46
HOMO − 6	b_{2g}	−7.37	b_{2u}	−7.35	a_g	−7.50
HOMO − 7	b_{1u}	−7.42	b_{1u}	−7.36	b_{2u}	−7.55

III. Results and Discussion

(a) Basis Set Effects. Table 1 shows the orbital energies and symmetries of 16 Kohn−Sham frontier orbitals of PH_2 for the VDZ, VDZP, and VTZP basis sets. For all the basis sets studied, the HOMO is b_{1u} ("a_{2u}" in D_{4h}) and the HOMO − 1 a_u ("a_{1u}" in D_{4h}), in agreement with DFT ΔSCF calculations which show the $^2B_{1u}$ state as the lowest ionized state of PH_2.[17−19] However, this ordering differs from that of *ab initio* Hartree−Fock calculations which yield an a_u HOMO and a b_{1u} HOMO − 1, regardless of the basis set.[20] Table 2 presents the DFT/SCI excitation energies and configurational composition of the nine lowest singlet states of PH_2 for different basis sets. It can be seen that both the symmetries and configurational composition of excited states are stable with respect to improvement of the basis set on going from VDZP to VTZP, but not on going from VDZ to VDZP, as shown in Table 2. Both Tables 1 and 2 show that the various results are converged with respect to the size of the basis set at the VDZP level, and accordingly, this basis set was chosen for all other calculations in this study. The change in the main configurations involved in going from VDZ to VDZP (see Table 2) is due to the change in energy ordering of the orbital symmetry of the HOMO and HOMO − 1.

(b) Excited States of Porphyrin. Table 3 presents the DFT/SCI/DZP, CASPT2,[3] SAC−CI,[4,5] STEOM-CCSD/DZP,[8] and gas-phase experimental singlet excitation energies for PH_2.[21] The two lowest DFT/SCI excitation energies of 2.03 and 2.29 eV are in excellent agreement with experimental Q band energies of 1.98 and 2.42 eV. In contrast, all the other calculations underestimate the lowest excitation energy compared to experiment (see Table 3). The Soret (B and N bands) and higher excitation energies are also well reproduced by our calculations. The calculated oscillator strengths are consistent with the large difference in extinction coefficients between the Q and Soret bands.

(c) Excited States of Hydroporphyrins. Table 4 and Figure 2 present the frontier orbital energies of PH_2, CH_2, BH_2, *cis*-IH_2, and *trans*-IH_2. As known from previous theoretical studies,[22,23] β-hydrogenation destabilizes the highest a_{1u}-type MO of PH_2 so that all the hydroporphyrins clearly have an a_{1u}-type HOMO. Table 5 presents the DFT/SCI, SAC−CI, and experimental[21,24−26] singlet excitation energies of the different hydroporphyrins.

Experimentally, the most obvious effect of ring hydrogenation is an intensification of the Q_x absorption band,[27] a feature that is reproduced in our calculations. The DFT/SCI oscillator strength of the first excited singlet state increases from 0.0005

TABLE 2: Excitation Energies[a] (eV) and Configurational Composition[b] of the Nine Lowest Singlet Excited States of PH_2 for Different Basis Sets

state	VDZ	main configuration	VDZP	main configuration	VTZP	main configuration		exp.
$1B_{3u}$	2.07 (0.0035)	59% (0−0) 39% (1−1)	2.03 (0.0005)	58% (0−1) 40% (1−0)	2.03 (0.0003)	57% (0−1) 42% (1−0)	Q_x	1.98
$1B_{2u}$	2.35 (0.00037)	53% (0−1) 45% (1−0)	2.29 (0.00000)	52% (0−0) 46% (1−1)	2.28 (0.00002)	51% (0−0) 47% (1−1)	Q_y	2.42
$2B_{3u}$	3.60 (0.5332)	53% (3−0) 30% (1−1) 13% (0−0)	3.54 (0.5451)	52% (3−1) 30% (1−0) 14% (0−1)	3.56 (0.6695)	57% (3−1) 31% (1−0) 17% (0−1)	B	3.83
$2B_{2u}$	4.01 (1.4457)	37% (1−1) 33% (0−1) 23%(3−1)	3.94 (1.3729)	36% (1−1) 33% (0−0) 24% (3−0)	3.89 (1.5269)	38% (1−1) 36% (0−0) 19% (3−0)		
$3B_{3u}$	4.39 (1.8003)	43% (3−0) 25% (1−1) 22% (0−0)	4.34 (1.7562)	45% (3−1) 24% (1−0) 22% (0−1)	4.29 (1.6175)	49% (3−1) 21% (1−0) 21% (0−1)	N	3.65
$3B_{2u}$	4.41 (0.8063)	71% (3−1) 11% (1−0)	4.34 (0.8293)	70% (3−0) 12% (1−1)	4.33 (0.7246)	76% (3−0) 10% (1−1)	L	4.25
$1B_{1u}$	4.59 (0.0040)	99% (5−1)	4.71 (0.0026)	99% (6−0)	4.80 (0.0022)	99% (7−0)		
$4B_{2u}$	4.88 (0.3943)	87% (7−1)	4.81 (0.3727)	87% (7−0)	4.81 (0.2859)	90% (5−0)	L	4.67
$4B_{3u}$	5.08 (0.2383)	95% (7−0)	5.06 (0.2145)	95% (7−1)	5.06 (0.2032)	95% (5−1)	M	5.50

[a] Oscillator strengths are given in parentheses. [b] Only configurations contributing more than 10% to a particular state are included. In the descriptions of the excitations shown in parentheses, the HOMO and LUMO are represented by 0, the HOMO − 1 and LUMO + 1 by 1, etc.

TABLE 3: Comparison of Excitation Energies[a] (eV) with DFT/SCI and Other Levels of Theory and Experiment

		exptl[21]	CASPT2[3] VDZ	SAC−CI[4] VDZ	SAC−CI[5] VDZP+Ry	STEOM-CC[8] DZP	DFT/SCI VDZP
Q_x	$1B_{3u}$	1.98 (0.01)	1.70 (0.001)	1.75 (0.0001)	1.81 (0.0028)	1.75 (0.0007)	2.03 (0.0005)
Q_y	$1B_{2u}$	2.42 (0.06)	2.26 (0.016)	2.23 (0.0006)	2.10 (0.0163)	2.40 (0.0013)	2.29 (0.0002)
B	$2B_{3u}$	3.33 (1.15)	2.91 (1.66)	3.56 (1.03)	3.47 (0.901)	3.47 (0.693)	3.54 (0.5451)
B/N	$2B_{2u}$		3.04 (1.54)	3.75 (1.73)	3.69 (1.88)	3.62 (1.20)	3.94 (1.3729)
N	$3B_{3u}$	3.65 (<0.1)		4.24 (0.976)	4.23 (1.63)	4.06 (0.931)	4.34 (1.7562)
L	$3B_{2u}$	4.25 (∼0.1)		4.52 (0.350)	4.40 (0.578)	4.35 (0.422)	4.34 (0.8293)
L	$4B_{2u}$	4.67 (∼0.1)		5.31 (0.280)		5.00 (0.153)	4.81 (0.3727)
M	$4B_{3u}$	5.50 (∼0.3)		5.45 (0.351)		5.17 (0.272)	5.06 (0.2145)

[a] Oscillator strengths are given in parentheses.

TABLE 4: Orbital Energies (eV) of the Six Frontier Orbitals of PH_2, CH_2, BH_2, *cis*-IH_2, and *trans*-IH_2

	LUMO + 2	LUMO + 1	LUMO	HOMO	HOMO − 1	HOMO − 2
PH_2	−0.80	−2.37	−2.39	−5.25	−5.52	−6.44
CH_2	−0.03	−1.80	−2.34	−5.03	−5.23	−6.33
BH_2	0.54	−1.01	−2.33	−4.55	−5.14	−6.76
cis-IH_2	0.56	−1.35	−2.00	−4.67	−5.10	−6.82
trans-IH_2	0.57	−1.49	−1.85	−4.57	−5.25	−6.05

TABLE 5: Excitation Energies[a] (eV) and Configurational Composition[b] of the Lowest Singlet Excited States of CH_2 BH_2 *cis*-IH_2, and *trans*-IC_2

	symmetry	exptl	SAC−CI[6]	DFT/SCI	main configuration
CH_2		(24[c])			
Q_x	$1B_1$	1.98 (0.10)	1.68 (0.0624)	2.09 (0.0647)	59% (0−0) 39% (1−1)
Q_y	$2A_1$	2.29 (0.06)	2.39 (0.0080)	2.35 (0.0014)	53% (1−0) 45% (0−1)
B	$2B_1$	3.18 (0.96)	3.58 (1.28)	3.58 (0.6800)	36% (1−1) 28% (2−1) 21% (0−0)
	$3A_1$		3.74 (1.68)	3.81 (0.3971)	65% (2−0) 14% (0−1) 13% (1−0)
	$4A_1$			4.09 (1.2760)	31% (2−0) 28% (0−1) 19% (1−0) 12% (0−2)
BH_2		(25[d])			
Q_x	B_{3u}	1.6 (m)	1.47 (0.188)	2.04 (0.2487)	71% (0−0) 27% (1−1)
Q_y	B_{2u}	2.3 (m)	2.42 (0.0257)	2.42 (0.0290)	59% (1−0) 40% (0−1)
B_y	B_{2u}	3.1 (sh)	4.11 (1.86)	4.27 (2.1260)	54% (0−1) 33% (1−0)
B_x	B_{3u}	3.4 (s)	4.24 (2.11)	4.45 (2.5780)	70% (1−1) 24% (0−0)
cis-IH_2		(26[e])			
Q_x	$1B_1$	1.95 (w)		2.14 (0.0949)	63% (0−0) 35% (1−1)
Q_y	$2A_1$	2.38 (w)		2.47 (0.0014)	53% (1−0) 45% (0−1)
B_y	$3A_1$	3.15 (s)		3.75 (1.1697)	44% (0−1) 38% (1−0)
B_x	$2B_1$	3.41 (s)		4.15 (1.4128)	45% (1−1) 20% (0−0) 13% (6^f-0) 11% (4^f-0)
trans-IH_2		(26[e])			
Q_x	$2A'$	2.17 (w)		2.26 (0.0914)	46% (0−0) 23% (1−1) 15% (0−1) 14% (1−0)
Q_y	$3A'$	2.31 (w)		2.42 (0.0724)	42% (0−1) 27% (1−0) 22% (0−0) 7% (1−1)
B_y	$4A'$	3.25 (s)		3.40 (0.2747)	54% (2−0) 22% (1−0) 17% (0−1)
B_x	$5A'$	3.35 (s)		3.72 (0.7874)	36% (1−1) 19% (2−0) 12% (1−0) 12% (0−0)
	$6A'$			4.01 (1.0462)	23% (2−0) 23% (1−1) 12% (1−0)

[a] Oscillator strengths are given in parentheses. Experimental intensities in parentheses with w = weak, m = medium, s = strong, and sh = shoulder. [b] Only configurations contributing more than 10% to a particular state are included. In the descriptions of the excitations shown in parentheses, the HOMO and LUMO are represented by 0, the HOMO − 1 and LUMO + 1 by 1, etc. [c] In benzene. [d] Data for bacteriophorbide. [e] In *n*-octane. [f] a_2 symmetry.

(PH_2) to 0.0647 (CH_2) and 0.2487 in BH_2, in qualitative agreement with experiment. Thus, the B/Q_x oscillator strength ratio decreases from approximately 2700 for PH_2 to 25 for CH_2 to 10 for BH_2. For these aromatic tetrapyrroles, the first excited singlet state is of mixed $a_u \rightarrow b_{2g}$ and $b_{1u} \rightarrow b_{3g}$ character (for D_{2h} symmetry labels), with the weight of the $a_u \rightarrow b_{2g}$ excitation increasing with increasing β-hydrogenation. The quasidegeneracy of the HOMO/HOMO - 1 and LUMO/LUMO + 1 for PH_2 is relaxed for CH_2 and further relaxed for BH_2. Thus, the transition moments for the two main configurations contributing to the S_1 state of PH_2 are of comparable size (58:40) for PH_2 and cancel each other out. In contrast, the transition moments for the two main configurations contributing to the S_1 state of hydroporphyrins cancel incompletely, as originally proposed by Weiss,[28] which explains the relatively intense Q_x feature of hydroporphyrins. The DFT/SCI results for BH_2 should not be compared with the experimental data in Table 5 in a straightforward manner, because the latter refer to bacteriopheophorbide, not BH_2. The first excited singlet state (S_1) of *trans*-IH_2 is blue-shifted relative to the S_1 of *cis*-IH_2 (Table 5), in qualitative agreement with experimental results[26] on the two

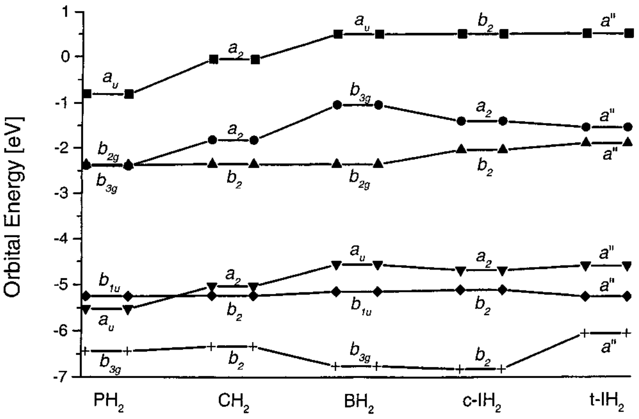

Figure 2. Orbital energy levels and symmetry of the six frontier orbitals of PH_2, CH_2, BH_2, *cis*-IH_2, and *trans*-IH_2.

tautomers whose ground states are essentially equienergetic.[23] Finally, the calculated Q_y and B-band energies also appear to be in reasonable agreement with experiment, although it remains to be explored whether DFT/MRCI calculations permit even better agreement between theory and experiment.

IV. Conclusions

DFT/SCI calculations provide an economical means for calculations of the excitation energies of porphyrin-type molecules with reasonable accuracy. The calculations reproduce the experimentally observed Q−B energy splitting in tetrapyrrole spectra and the intensification, relative to porphyrin, of the Q_x band of hydroporphyrins. In a number of instances, the DFT/CI results agree significantly better with experiment than SAC−CI results. Far less computationally demanding than CASPT2 calculations, DFT/SCI calculations are readily extended to larger and more complex systems such as substituted porphyrins and transition metal porphyrins as well as to photobiological applications.[29]

Acknowledgment. We thank the German Academic Exchange Service (DAAD) for a Postdoctoral Fellowship (A.B.J.P.), Stefan Grimme (University of Bonn, Germany) for valuable advice, the Norwegian Research Council (A.G., A.B.J.P.), and the San Diego Supercomputer Center for a Senior Fellowship (A.G.).

References and Notes

(1) Ghosh, A. *Acc. Chem. Res.* **1998**, *31*, 189.

(2) Ghosh A. Quantum Chemical Studies of Molecular Structures and Potential Energy Surfaces of Porphyrins and Hemes. *The Porphyrin Handbook*; Academic Press: New York, 2000; Vol. 7, pp 1−38.

(3) Merchán, M.; Ortí, E.; Roos, B. O. *Chem. Phys. Lett.* **1994**, *226*, 27.

(4) Nakatsuji, H.; Hasegawa, J.; Hada, M. *J. Chem. Phys.* **1996**, *104*, 2321.

(5) Kitao, O.; Ushiyama, H.; Miura, N. *J. Chem. Phys.* **1999**, *110*, 2936.

(6) Hasegawa, J.; Ozeki, Y.; Hada, M.; Nakatsuji, H. J. *Phys. Chem. B* **1998**, *102*, 1320.

(7) Nooijen, M.; Bartlett, R. J. *J. Phys. Chem.* **1997**, *106*, 66449.

(8) Gwaltney S. R.; Bartlett, R. J. *J. Chem. Phys.* **1998**, *108*, 6790.

(9) Bauernschmitt, R.; Ahlrichs, R. *Chem. Phys. Lett.* **1996**, *256*, 454.

(10) Grimme, S. *Chem. Phys. Lett.* **1996**, *259*, 128.

(11) Ahlrichs, R.; Bär, M.; Häser, M.; Horn, H.; Kölmel, C. *Chem. Phys. Lett.* **1989**, *162*, 165.

(12) Treutler, O.; Ahlrichs, R. *J. Chem. Phys.*, **1995**, *102*, 346.

(13) Dunning, T. H.; Hay, P. J. In *Modern Theoretical Chemistry*; Schaefer, H. F., III, Ed.; Plenum Press: New York, 1977; Vol. 3.

(14) Becke, A. D. J. Chem. Phys. **1993**, *98*, 5648.

(15) Stephens, P. J.; Devlin, F. J.; Chabalowski, C. F.; Frisch, M. J. *J. Phys. Chem.* **1994**, *98*, 11623.

(16) Schäfer, A.; Horn, H.; Ahlrichs, R. *J. Chem. Phys.* **1992**, *97*, 257.

(17) Ghosh, A.; Almlöf, J. *Chem. Phys. Lett.* **1993**, *213*, 519.

(18) Ghosh, A. *J. Am. Chem. Soc.* **1995**, *117*, 4691.

(19) Ghosh, A.; Vangberg, T. *Theor. Chem. Acc.* **1997**, *97*, 143.

(20) Ghosh, A.; Almlöf, J.; Gassman, P. G. *Chem. Phys. Lett.* **1991**, *186*, 113.

(21) Edwards, L.; Dolphin, D. H.; Gouterman, M.; Adler, A. D J. *Mol. Spectrosc.* **1971**, *38*, 16.

(22) Gouterman, M. In *The Porphyrins*; Dolphin, D., Ed.; Academic Press: New York, 1978; Vol. III, Part A, Physical Chemistry.

(23) Ghosh, A *J. Phys. Chem.* **1997**, *101*, 3290.

(24) Nagashima, U.; Kashiwagi, T.; Takada, H.; Nakamura, H. *J. Chem. Phys.*, **1986**, *85*, 4524.

(25) Scheer, H.; Inhoffen, H. H. In *The Porphyrins*; Dolphin D., Ed.; Academic Press: New York, 1978; Vol. III, Part A, Physical Chemistry.

(26) Huang, W.-Y.; Wild, U. P.; Johnson, L. W. *J. Phys. Chem.* **1992**, *96*, 6189.

(27) Chang, C. K. *Biochemistry* **1980**, *19*, 1971.

(28) Weiss, C. In *The Porphyrins*; Dolphin D., Ed.; Academic Press: New York, 1978; Vol. III, Part A, Physical Chemistry.

(29) Hermann, D. T.; Schindler, A. C.; Polborn, K.; Gommper, R.; Stark, S.; Parusel, A. B. J.; Grabner, G.; Köhler, G. *Chem. Eur. J.* **1999**, *5*, 3208.