A spectroscopic and computational study of the singlet and triplet excited states of synthetic \( \beta \)-functionalized chlorins


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Abstract

This paper presents a comparative investigation of the absorption, fluorescence, electron paramagnetic resonance (EPR), and transient triplet–triplet absorption spectroscopic properties and triplet state dynamics of two functionalized, synthetic, \( \textit{meso} \)-phenylchlorins. The chromophores investigated are the novel 2-hydroxy-3-oxa-5,10,15,20-tetrakisphenylchlorin (3) and the known 2,3-dioxo-5,10,15,20-tetrakisphenylchlorin (4). In these chromophores, one peripheral \( \textit{\textit{\( \beta \)}} \)-CH\( = \)CH\( = \) bond of the parent porphyrin \( \textit{meso} \)-tetrakisphenylporphyrin (TPP, 1) was formally replaced by a \( \textit{\textit{\( \beta \)}} \)-CH(OH)O\( = \) (lactol) or a \( \textit{\textit{\( \beta \)}} \)-diketone moiety. The spectroscopic data are compared with results from investigations on the parent porphyrin TPP studied here and the parent chlorin 5,10,15,20-tetrakisphenylchlorin (TPC, 2) from the literature. The spectroscopic observables are examined both qualitatively within the framework of the four orbital model and quantitatively using MNDO-PSDCI methods. The results delineate the role of \( \textit{\textit{\( \beta \)}} \)-lactol and \( \textit{\textit{\( \beta \)}} \)-dicarbonyl moieties in controlling the electronic and spectroscopic properties of these chromophores. This investigation serves as the foundation from which to derive a general understanding of the effects of \( \textit{\textit{\( \beta \)}} \)-functionalization on the electronic properties of chlorin-type chromophores. This knowledge is required for the design and understanding of long-wavelength absorbing and fluorescing chromophores to be used in light harvesting systems and photomedicine.

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Abbreviations: EPR, electron paramagnetic resonance; HOMO, highest occupied molecular orbital; LUMO, lowest unoccupied molecular orbital; MO, molecular orbital; TPP, \( \textit{\textit{\( \textit{\textit{\( \beta \)}} \)}} \textit{\textit{\( \textit{\textit{\( \beta \)}} \)}} \textit{\textit{\( \textit{\textit{\( \beta \)}} \)}} \textit{\textit{\( \textit{\textit{\( \beta \)}} \)}} \)-tetraphenylporphyrin (5,10,15,20-tetrakisphenylporphyrin); TPC, \( \textit{\textit{\( \beta \)}} \)-tetraphenylchlorin (5,10,15,20-tetrakisphenylchlorin).

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1. Introduction

Porphyrins and chlorins (β, β'-dihydroporphyrins) [1] possess planar, rigid, aromatic, π-electron systems that are responsible for many of their electronic and spectroscopic properties. The π-system of porphyrins is comprised of a central, 18 π-electron system in conjugation with two cross-conjugated β, β'-double bonds (Fig. 1(a)). Removal of one of these β, β'-double bonds generates a chlorin [1]. This modification has a number of consequences on the electronic structure and spectroscopic properties of the resulting chromophore [1,2].

![Figure 1](https://example.com/fig1.jpg)

Fig. 1. A schematic representation of the structures (a), two highest occupied and two lowest unoccupied molecular orbitals (b), and electronic states (c) of porphin and chlorin.

The spectroscopic features of porphyrins and chlorins can be understood in large part by considering the energies and electronic distributions of the two highest occupied molecular orbitals (HOMOs) and the two lowest unoccupied molecular orbitals (LUMOs) [3]. For a porphyrin possessing D₄h symmetry (e.g., a metalloporphyrin), the pair of LUMOs are degenerate by symmetry and labeled eₓ and eᵧ. The pair of HOMOs are designated a₁u and a₂u, and are degenerate [3]. Electronic states resulting from optical transitions between the orbitals a₁u → eₓ and a₂u → eᵧ are ɣ-polarized, and to first order. They have the same energy as optical transitions between the orbitals a₂u → eₓ...
molecular orbitals (MOs), bonded to two opposing central nitrogens. The transitions induced by the reduction of one model.

In the following text, we shall exclusively use the cant amount of electron density on the $b_1$ and $b_2$ point group ($Q_b$ and $Q_y$) owing to the presence of two hydrogens morphore porphin (Fig. 1(a)) have lower symmetry $b_1$ and $b_2$ respectively (Figs. 1(b) and (c)). In molecules having $D_{2h}$ symmetry, the $x$ molecular axis (defined here as through the central nitrogen electron lone pairs) and the $y$ molecular axis (through the central N–H bonds) are not equivalent (Fig. 1(a)). Thus, the excited states resulting from transitions between the orbitals are not degenerate, and the spectroscopic transitions are expected to be split into distinct $x$ and $y$ bands (Figs. 1(b) and (c)) with the $Q$ transitions becoming allowed. Reducing one of the two $\beta, \beta'$-double bonds of the porphin chromophore to form a chlorin or adding functional groups to its periphery likewise lowers its symmetry (Fig. 1(a)). For systems of symmetry lower than $D_{2h}$, a generalized notation for the MOs has been adopted with $b_1$ and $b_2$ corresponding to the HOMOs $a_{1u}$ and $a_{2u}$ in the $D_{4h}$ point group ($a_u$ and $b_{1u}$ in the $D_{2h}$ point group), and $c_1$ and $c_2$ corresponding to the LUMOs $e_{gx}$ and $e_{gy}$ in the $D_{4h}$ point group ($b_{3g}$ and $b_{2u}$ in the $D_{2h}$ point group), respectively (Figs. 1(b) and (c)). In the following text, we shall exclusively use the $b_1$, $b_2$, $c_1$, $c_2$ generalized notation for the 4-orbital model.

The effects on the energy levels and optical transitions induced by the reduction of one $\beta, \beta'$-double bond to form a chlorin from porphin are rationalized by considering the electron distribution of the MOs (Fig. 2). Reduction of a pyrrole ring will preferentially destabilize the $b_2$ and $c_1$ orbitals (Fig. 1(b)) because they locate a significant amount of electron density on the $\beta, \beta'$-carbons affected by the structural modification (Fig. 2). The $b_1$ and $c_2$ orbitals are not changed to any significant degree because they possess only minimal electron density on the relevant $\beta, \beta'$-carbons.

Owing to distinct differences in the chemical reactivity of the cross-conjugated $\beta, \beta'$-double bonds, and which can be characterized as pseudo-olefinic compared to the bonds of the central, aromatic $\pi$-electron system, the synthesis of novel functionalized chlorins and chlorin-like chromophores can be achieved [1,4–9]. These modifications affect the symmetry and electronic distribution of the parent chromophores, yet the electronic consequences of these functionalizations compared to chlorins generated by simple hydrogenation of a $\beta, \beta'$-double bond [10,11] have not been fully explored. The desire to design long-wavelength absorbing and fluorescing chromophores is a main driving force in current porphyrin chemistry because these chromophores would fulfill the photophysical requirements for their effective use in photomedicine [12–14]. Therefore, a comprehensive understanding of the structure–electronic properties relationship of these chlorin-type chromophores is needed.

We have begun a comparative investigation of the spectroscopic properties of selected, synthetic, meso-phenyl-chlorins and -chlorin-like macrocycles. The behavior of two such molecules is reported here. These are 2-hydroxy-3-oxa-5,10,15,20-tetakisphenylchlorin (3) and 2,3-dioxo-5,10,15,20-tetakisphenylchlorin (4) whose structures are shown in Fig. 3 along with the parent chromophores 5,10,15,20-tetakisphenylporphyrin (1, TPP) and 5,10,15,20-tetakisphenylchlorin (2, TPC). Comparing the absorption, fluorescence, electron paramagnetic resonance (EPR), transient triplet–triplet absorption spectra, and dynamics of the excited triplet states of the molecules allows us to evaluate the electronic effects that functionalization of the chromophores has on their $\pi$-electron systems. The spectroscopic observables are examined both qualitatively and quantitatively using MNDO-PSDCI methods [15–18]. These studies provide the framework from which to understand the role of phenyl groups as well as hydroxyl or carbonyl substituents in controlling the electronic and spectroscopic properties of the entire class of $\beta$-functionalized chlorin-type chromophores.
Fig. 2. Molecular orbitals of the two highest energy filled and two lowest energy unfilled orbitals of porphin and chlorin. The orbitals were generated using Gaussian 98 based on a density functional calculation (B3LYP) using a 6-31G(d) basis set (see text). The energies are given in atomic units (1 Hartree = 27.2114 eV).
2. Materials and methods

2.1. Synthesis

2.1.1. Materials and analysis

Porphyrin 1 [19], 2,3-dihydroxy-5,10,15,20-tetakisphenylporphyrin (5) [20,21] and 2-oxa-3-oxo-5,10,15,20-tetrakisphenylporphyrin (porpholactone, 6) [9] were prepared according to literature procedures (Scheme 1). All chemicals (Aldrich) and solvents used were of analytical purity or better. The silica gel used for flash chromatography was Silica Gel 60, 32–63 μm (Sorbent Technologies, Atlanta, GA). Rf-values were measured on Merck silica TLC aluminum sheets (silica gel 60 F254).

1H NMR and 13C NMR spectra were measured on a Bruker instrument and were referenced to residual solvent peaks. ESI mass spectra were obtained on a Micromass Quattro II. High resolution FAB mass spectra were provided by the Mass Spectrometry Facility, Department of Chemistry and Biochemistry, University of Notre-Dame (Bill Boggess). Elemental analyses were performed by NuMega Resonance Labs, Inc., San Diego, CA.

2.1.2. 2-Hydroxy-3-oxa-5,10,15,20-tetakisphenylchlorin (3)

Porpholactone 6 (400 mg) is converted quantitatively into the corresponding Zn(II) complex by heating a solution in CHCl3/10% MeOH (50 mL) and 2 equiv Zn(OAc)2·C12H2O to reflux for 30 min. The solution is then washed three times with H2O, the organic phase dried (MgSO4) and evaporated to dryness. The residue is passed through a short column of silica gel (CH2Cl2). The main green-purple fraction (Zn II-complex of 6) is collected and evaporated to dryness and used without further purification in the next step. Rf = 0.82 (silica–ethyl acetate:hexane 3:1); UV–vis (CH2Cl2) λmax: 402 (sh), 422, 520, 558, 602. The zinc complex (200 mg) is dissolved in dry THF (20 mL) under anhydrous conditions and the solution is cooled to −78 °C. DIBAL-H (20% in hexane, 1.0 mL, 9.8 × 10−4 mol, 7.0 equiv) was added by syringe, and the reaction mixture was warmed to room temperature.
temperature and allowed to stir for an additional hour. The reaction was then quenched by addition of a few drops of H₂O, washed twice with 6 M aq HCl (this demetallates the chromophore), followed by an aq NaHCO₃ solution, and finally H₂O. The organic phase was isolated, dried over anhydrous MgSO₄, and evaporated to dryness. The residue was purified by flash chromatography (silica–CH₂Cl₂). The main fraction (red) was collected, and its volume reduced by rotary evaporation. A slow solvent exchange with cyclohexane provides 3 as a purple powder of analytical purity in 90% yield.

Rf = 0.54 (silica–CH₂Cl₂); UV–vis (CHCl₃) \( \lambda \max (\log e) \): 416 (5.26), 515 (4.12), 550 (4.18), 593 (3.88), 646 (4.52) nm; Fl (CHCl₃, \( \lambda \) excitation = 420 nm) \( \lambda \max (\text{rel. intensity}) \): 651 (1.0), 701 (0.07) nm; \(^1\)H NMR (400 MHz, CDCl₃, \( \delta \)): 8.59 (d, \( J = 2.4 \) Hz, 1H), 8.52 (d, \( J = 2.3 \) Hz, 1H), 8.43 (d, \( J = 2.3 \) Hz, 1H), 8.35 (d, \( J = 2.3 \) Hz, 1H), 8.18 (d, \( J = 2.3 \) Hz, 1H), 8.11 (m, 6H), 7.87 (m, 2H), 7.71 (m, 12H), 3.62 (d, \( J = 3.6 \) Hz, 1H), ppm; ESI-MS (70 V, 100% CH₃CN, \( m/z \)): 635 (MH⁺); HR-MS (+FAB of MH⁺) calc’d for C₂₁₃₉₃N₄O₂: 634.2368, found: 634.2373.

2.1.3. 2,3-Dioxo-5,10,15,20-tetrakisphenylchlorin (4)

A solution of diol 5 (165 mg, 2.55 × 10⁻⁴ mol) in benzene (22 mL) and pyridine (3 mL) was heated to reflux for 36 h during which time DDQ (270 mg, 6.5 eq) was added in three equal increments. Caking in the flask during the reaction was removed by sonication. Once all starting material was consumed (tlc control), the solvent was evaporated under vacuum. The residue was taken up in CH₂Cl₂ and filtered through a plug of silica gel. The filter cake was extracted with CH₂Cl₂ until the filtrate was nearly colorless. The filtrate was reduced and 4 was isolated and purified by column chromatography (silica, CHCl₃/20% pet ether 30–60). The main brown fractions were combined and evaporated to dryness, depositing a dark blue powder of analytical purity (120 mg, 73%). Rf = 0.6 (silica–CH₂Cl₂); UV–vis (CHCl₃) \( \lambda \max (\log e) \): 403 (4.87), 475 (3.84) nm; Fl (CHCl₃, \( \lambda \) excitation = 420 nm) \( \lambda \max (\text{rel. intensity}) \): 648 (1.0), 708 (0.2) nm; \(^1\)H NMR (400 MHz, CDCl₃, \( \delta \)): 8.78 (d, \( J = 5.0 \) Hz, 2H), 8.64 (d, \( J = 5.0 \) Hz, 2H), 8.60 (s, 2H), 8.16 (d, \( J = 7.5 \) Hz, 4H), 7.94 (d, \( J = 7.5 \) Hz, 4H), 7.82–7.70 (m, 12H), −1.9 (br s, 2H); \(^1\)C NMR (100 MHz, CDCl₃, \( \delta \)): 187.8, 141.0, 140.7, 139.8, 139.2, 138.1, 134.2, 134.1, 132.6, 128.4, 128.2, 128.1, 128.0, 127.1, 126.9, 124.0, 114.0; MS (ESI, 100% CH₃CN, \( m/e \)): 645 (MH⁺, 70), 683 (MK⁺, 100); HR-MS (+FAB of MH⁺) calc’d for C₄₄H₃₆N₄O₂: 644.2212, found: 644.2220.
2.2. Absorption and fluorescence spectroscopy

Absorption spectra were recorded on Cary 50 and fluorescence spectra on a Cary Eclipse spectrophotometer at room temperature in the solvents indicated in the figures.

2.3. Transient triplet–triplet absorption spectroscopy

Samples were prepared for transient triplet–triplet absorption by dissolving the molecules in either toluene (99.8% HPLC grade, Fisher Scientific) or 2-methyltetrahydrofuran (2-MTHF, 99+% anhydrous, Aldrich), placing them in 1 cm cuvettes fitted with a vacuum stopcock, and subjecting them to at least five freeze–pump–thaw cycles. The triplet state dynamics of all of the molecules were significantly faster in the presence of oxygen. The samples required thorough degassing for the triplet lifetimes to converge to their inherently slower values. The experiments were performed at room temperature using excitation from a Quanta-Ray Pro-230/MOPO-710 Nd:YAG-pumped optical parametric oscillator laser tuned to 590 nm and having a pulse repetition rate of 9.8 Hz and an output energy of 8.7 mJ. The laser beam was focused onto the sample at a right angle to the measuring beam which consisted of an Oriel 150 W Xe arc lamp filtered by a 40% transmitting neutral density filter. The light transmitted through the sample was passed through an Instrument SA model LH290 1200 g/mm monochromator and focused onto a photodiode detector. The output was then amplified using a home-built amplifier and fed to a Tektronix digital oscilloscope model TDS 620A for signal averaging. Each transient profile consists of an average of 5000 scans.

2.4. EPR spectroscopy

Approximately 0.6 mg of 1, 3 or 4 was dissolved in 0.5 mL of 10:1 (v/v) toluene (99.8% HPLC grade, Fisher Scientific):pyridine (99.9% ACS grade, JT Baker). All samples were degassed prior to the experiments by subjecting them to at least five freeze–pump–thaw cycles. Triplet state EPR spectroscopy was performed using a Bruker EMX X-band spectrometer with WIN-EPR acquisition software v.3.01. The sample temperature was maintained near 4.2 K using a continuous flow liquid helium cryostat (ESR 900) and monitored with a temperature controller (Oxford ITC4). Excitation was provided by light from a 1000 W Xe arc lamp (Kratos LH151N/1S) filtered by 5 cm of water in a pyrex bottle and passed through 2 focusing lenses onto the sample in the cavity. The instrument settings for all spectra were as follows: Signal channel: modulation amplitude, 20 G; center field, 3340 G; time constant, 327.68 ms; scan width, 1000 G; receiver gain, 1.12 × 10^5; microwave frequency, 9.3 ± 0.1 GHz; conversion time, 327.68 ms; sweep time, 167.77 s; field resolution, 512 points; and number of scans, 8. A spectral trace of each sample under continuous illumination was taken followed by another spectrum with the light off. Light-minus-dark difference spectra were obtained by subtraction using the Bruker WIN-EPR system software v.2.11. The zero-field splitting parameters were obtained directly from the spectral traces assuming 2|D| for the splitting between the outmost peaks, |D| − 3|E| for the splitting between the innermost peaks, and |D| + 3|E| for the splitting between the intermediate peaks.

2.5. Theoretical methods

2.5.1. Molecular geometries

Ground state geometries were calculated for vacuum conditions using density functional methods with semiempirical (AM1) geometries as starting guesses. We adopted Becke’s three-parameter exchange functional together with the correlation functionals of Lee–Yang–Parr (B3LYP) [22–27] and a 6-31G(d) basis set as implemented within Gaussian 98 [28]. The corresponding unrestricted (open shell) B3LYP density functional method and a 6-31G(d) basis set were used to calculate the excited state T1 geometry. The initial guess coordinates for the triplet density functional calculations were generated from open shell Hartree–Fock calculations. Gaussian 98 was run on our 16-node Beowulf cluster (Western Scientific, San Diego, CA 92123) using Linda 6.2 (Scientific Computing
Associates, New Haven, CT 06510) software to handle distribution. Each node has two Pentium III 1.26 GHz processors, 1 GB RAM and runs Red Hat Linux 7.3. The ground state DFT calculations typically required 2–3 days with each calculation assigned six processors. The triplet excited state calculations took 3–6 days with each calculation assigned eight processors.

2.5.2. Spectroscopic properties

The energy and photophysical properties of the excited state singlet manifolds were analyzed by using the ground state geometries obtained from the density functional methods. Both ZINDO [29–31], as implemented within Quantum Cache 4.9, and MNDO-PSDCI [15–18] methods were used for comparison. The ZINDO calculations included all singly excited configurations generated from the 18 highest energy occupied and the 18 lowest energy unoccupied MOs (324 singles). The MNDO-PSDCI calculations included all the single and double configurations generated from a restricted basis set of the eight highest energy occupied MOs and the eight lowest energy unoccupied MOs (64 singles and 2080 doubles). These MOs were selected from those localized within the porphyrin or chlorin macrocycle.

3. Results and discussion

3.1. Syntheses of chromophores 3 and 4

All of the molecules were synthesized starting from TPP (Scheme 1). Osmium tetroxide-mediated dihydroxylation of TPP generates known vic-diol chlorin 5 [20,21]. This reaction is one of the rare direct porphyrin-to-chlorin conversions. Unlike the better known reaction of this type, the diimide reduction of TPP [10,11] to generate chlorins of type 2, the functionalization of the \( \beta, \beta' \)-bond activates chlorin 5 for subsequent transformations. Oxidation of diol 5 using oxidative diol cleavage conditions (MnO\(_{4}^{-}\)) produces porpholactone 6 [9]. This synthesis of this intriguing molecule is a general alternative to established syntheses [32–36]. The initial permanganate-cleavage product is presumably the corresponding secoclorin bисcarбоксилate which spontaneously decarboxylates to form porpholactone 6. This mechanism of formation was also implied when 6 was first discovered by Crossley [32]. Coordination of 6 to Zn\(^{2+}\), followed by reduction with a hydride source (DIBAL-H) and subsequent acid-induced removal of the zinc ion, smoothly generates lactol 3 [9]. The metallation/demetallation sequence was necessary to protect the macrocycles from the adventitious formation of aluminum complexes during the reduction step. The ultimate result of these conversions is that one peripheral \(-\text{CH}=\text{CH}--\) bond of TPP was formally replaced by \(-\text{CH}(\text{OH})O--\) (lactol) moiety. Because the cross-conjugated double bond of TPP was removed and replaced by sp\(^{3}\)-hybridized atoms, a chlorin-like spectroscopic behavior for 3 is expected.

On the other hand, oxidation of diol 5 using dehydrogenating conditions (DDQ) provides 2,3-dioxochlorin 4. This method to synthesize this class of compounds is a simplified method complementary to established syntheses [32,38]. Diones such as 4 have found wide use in the construction of multi-porphyrin assemblies and porphyrins containing extended \( \pi \)-systems [38–40]. In the chromophore of 4, the peripheral \(-\text{CH}=\text{CH}--\) bond of TPP was replaced with an 1,2-diketone moiety. Thus, although the cross-conjugated \( \beta, \beta' \)-bond of porphyrins was removed, the sp\(^{2}\)-hybridization of the carbons involved was not changed. Further, two carbonyl bonds in conjugation with the central \( \pi \)-system were established, suggesting a strong electronic modulation of the chlorin chromophore.

3.2. Singlet states

3.2.1. Absorption and fluorescence spectroscopy

The absorption spectra of molecules 1–4 are given in Fig. 4. As expected from their structural features, the spectra of TPC 2 and lactol 3 are chlorin-like. The most striking differences in the absorption spectra of molecules 2 and 3 compared to 1 and 4 are broader peaks and substantial shoulders in the Soret region, and more intensity in the \( Q \)-bands for the chlorins 2 and 3 compared to the spectra of 1 and 4. Indeed, the bands in the \( Q \)-region of chromophores 2 and 3 are well developed, and those of TPP 1, while small, are
clearly resolved into four distinct peaks between 500 and 650 nm. However, although dione 4 displays a relatively narrow Soret band near 400 nm and an additional small absorption feature near 475 nm, only a long, sloping and featureless absorption profile at longer wavelengths is observed. Thus, the existence of \( \pi \)-electron conjugation with the carbonyl groups renders the absorption spectrum of this chromophore neither chlorin-like nor completely porphyrinic.

The fluorescence spectra of chromophores 1, 3, and 4 are also shown in Fig. 4 (dashed line). Lactol 3 displays the bathochromically shifted single-prominent vibronic band spectrum typical of chlorins. Molecules 1 and 4 show two distinct vibronic bands in their fluorescence spectra, which is typical of porphyrin-like behavior. Molecules 1 and 3 also display good mirror image symmetry with their respective Q-band absorptions. However, the fluorescence spectrum of 4 which peaks at 648 nm does not have good mirror image symmetry with its absorption spectrum. Nevertheless, the main fluorescence band is strong and has a well-defined Gaussian shape, suggestive of the presence of a low-lying excited singlet state at this energy. An absorption transition from the ground state into this state is evidently broadened beyond recognition.

The effects seen in these \( \text{meso} \)-phenyl substituted chromophores can be qualitatively understood in a similar manner as described in the introduction for the parent porphin chromophore. The introduction of electron donating phenyl groups at the methine carbons of porphin destabilizes the \( b_1 \) HOMO relative to the \( b_2 \) orbital, and destabilizes the LUMOs, \( c_1 \) and \( c_2 \) by approximately an equivalent amount. The overall effect is to remove the degeneracy of the states leading to a reduction in CI. In going from TPP 1, to TPC 2, the \( b_2 \) and \( c_1 \) MOs, which have electron density on the \( \beta, \beta' \)-carbons affected by the reduction, will be de-stabilized relative to the \( b_1 \) and \( c_2 \) MOs (Fig. 5). In TPP, the \( b_1 \) orbital is the HOMO, and \( b_2 \) is the HOMO-1 orbital. For TPC, these orbitals switch position, and the \( b_2 \) orbital becomes the HOMO, and \( b_1 \) becomes the HOMO-1 orbital (Fig. 5). Analogous to TPC, \( b_2 \) is the HOMO in lactol 3, but in dione 4, as in TPP, \( b_1 \) is the HOMO (Fig. 5). Saturating the \( \beta, \beta' \)-carbons reduces the extent of CI between the states and leads to a splitting of the \( x \)- and \( y \)-polarized transitions (Fig. 1(c)). This accounts for the broader peaks and shoulders seen in the Soret region for the chlorin 2 and chlorin-like chromophore 3. The increase in the transition probability of the \( Q_y \) transition for these molecules compared to the chromophores in 1 and 4 is also observed and is accounted for by the loss of CI between states of these chlorins formed by transitions.
Fig. 5. Molecular orbitals of the two highest energy filled and two lowest energy unfilled orbitals of molecules 1, 2, 3 and 4. The orbitals are arranged above the molecular diagrams. The orbitals were generated using Gaussian 98 based on a density functional calculation (B3LYP) using a 6-31G(d) basis set (see text). The orbital energies are given in atomic units (1 Hartree = 27.2114 eV).
involving electrons in non-degenerate orbitals. In dione 4, π-electron conjugation is imparted through the carbonyl groups which renders it distinctly non-chlorin-like and leads to diminished intensity in the Q bands.

Molecular orbital computations provide a more quantitative evaluation of the differences in electronic structure and absorption spectral profiles of the molecules. An analysis of the spectroscopic properties of molecules 1–4 based on MNDO-PSDCI theory is presented in Fig. 6. In general, the calculations do a reasonable job of predicting the Soret region and do a poor job of describing the Q-bands. This problem is also evident in the ZINDO-SCI calculations, but ZINDO does a better job of predicting the location and intensities of the Q bands than MNDO-PSDCI. In general, the porphyrins and the chlorins are well described by simple molecular orbital theory limited to single excitation configuration interaction [41–46]. The goal of the present computations is to provide additional perspective on these molecules as deduced from the MNDO-PSDCI theory, which includes full single and double CI within the selected 8 × 8 π-electron system.

Molecules 1 and 4 both display relatively sharp Soret bands which is characteristic of porphyrins and porphyrin-like system. The calculations indicate that the Bx and By transitions (Fig. 1(c)) in both molecules are nearly degenerate and are dominated by single excitations (HOMO → LUMO and HOMO → LUMO + 1). Note that there are two isoenergetic bands with identical oscillator strength (f = 1.02) represented by the single, tall vertical bar in the MNDO-PSDCI analysis of molecule 4 (Fig. 6). In all cases, the Bx and By transitions are well described by single excitations, and have only 18% doubly excited character. More interestingly, the low-lying weak Q bands have virtually no doubly excited character (<10%). This observation explains why the semi-empirical methods limited to single CI do such a

Fig. 6. Comparison of the absorption spectra of 1–4 with the one-photon properties as calculated by using MNDO-PSDCI molecular orbital theory. The height of the vertical bar is proportional to the calculated oscillator strength, dark lines are transitions dominated by single excitations and gray lines indicate transitions with significant doubly excited character. Dark lines that are dashed indicate a significant charge transfer character. In selected cases, the percentage of doubly excited character is indicated using the symbol D.
competing job at describing the low-lying transitions of the porphyrins and chlorins [41–46].

MND0-PSDCI theory, however, does offer some new insights into the electronic spectra of porphyrins and chlorins. There is a relatively strong transition predicted at a slightly higher energy than the Soret band in TPC that is dominated by a HOMO → LUMO + 2 single excitation. The MND0-PSDCI calculations predict that this state has significant doubly excited character. As shown in Fig. 6, a vibronic band in TPC is observed in close proximity to the predicted energy. (The corresponding transition in molecule 3 is also predicted to be relatively strong.) Surprisingly, this state is predicted to lie below the Soret band at about 22.1 kK in molecule 4. A vibronic band in the absorption spectrum of molecule 4 (Fig. 6) is in good agreement with the predicted energy, providing further support for the assignment. To our knowledge this is the first time this vibronic feature, which is present in most chlorins, has been given a firm assignment. We note further that this state is not properly described within the simple four orbital model.

Molecule 4 is calculated to have a Soret band more like a porphyrin than like a chlorin in good agreement with observation. Both molecules 1 and 4 are predicted to have very sharp Soret bands due to the fact that the $b_1 \rightarrow c_1$ and $b_1 \rightarrow c_2$ transitions are expected and calculated to have nearly identical energies.

3.3. Triplet states

3.3.1. Transient triplet–triplet absorption spectra and dynamics

Upon excitation of molecules 1, 3 and 4 with a laser pulse, similar transient absorption spectra are obtained (Fig. 7). There is a rapid onset of bleaching of the ground state absorption observed in the region of the Soret band between ~400 and 430 nm and an absorption increase detected in the range ~430 and 500 nm (Fig. 7). The absorption increase is associated with triplet–triplet absorption originating from the lowest excited triplet state of the molecules. The dynamics of the decay of the triplet–triplet absorption and the recovery of the bleached signal were the same within experimental error for each of the molecules, and independent of pump and probe light wavelength and intensity and sample concentration. A fit to a single exponential rate equation of the transient response curves obtained from the deoxygenated samples yielded triplet state lifetimes of 1.15 ± 0.05 ms for TPP 1, 440 ± 60 µs for 3 and 310 ± 10 µs for 4. The triplet state lifetime for TPC was reported in the literature to be 4.4 ± 0.6 ms based on the average of the rate constants of decay of the three individual triplet spin sublevels [47]. All the dynamics values are summarized in Table 1.

The dynamics of intersystem crossing (isc) from the triplet state of π-electron systems to the ground state are governed largely by non-radiative processes where the rate constant of depopulation of spin sublevel $i$ in triplet state $T_i$ into an isoenergetic vibrational level of the ground state $S_{0v}$ can be expressed as

$$k_{isc} \langle T_i \rightarrow S_0 \rangle = \frac{2\pi}{\hbar} \left| \left\langle T_i | H_{int} | S_{0v} \right\rangle \right|^2 \rho(E),$$

where $H_{int}$ is the perturbation operator responsible for driving population from the triplet state to the ground state and $\rho(E)$ is the density of final states into which isc proceeds. The above expression can be manipulated for calculation of the $k_{isc}$ rate constants of the individual triplet spin sublevels. This requires substituting appropriate wavefunctions and operators and then carrying out a perturbation theory expansion of the resulting integral [47–54].

One of the most important features of this model is that it illustrates the importance of $\sigma\pi^*$ or $n\pi^*$ states in controlling the rate of depopulation of the triplet state. This is because for a $\pi\pi^*$ triplet state, the most important spin–orbit coupling terms for isc involve one-center mixing with singlet states derived from $\sigma\pi$ configurations [55,56]. The lowest energy $\sigma\pi$ states will be the most important because the isc expressions have a denominator representing the energy difference between the mixing states. Among the most available $\sigma\pi$ states are those involving non-bonding electrons centered on the pyrrole nitrogen atoms or, in the case of dione 4, those associated with the carbonyl oxygens. If the principal magnetic axes for molecules TPP, TPC and lactol 3, are defined as shown
in Fig. 1, the non-bonding electrons on the pyrrole nitrogens point along the $x$-axis. Because the $1n\pi^*$ states are derived from these orbitals, they will be spin–orbit coupled to the $\pi\pi^*$ triplet state by spin–orbit operators directed along the $y$-axis [57,58]. The spin sublevel associated with the $x$-axis direction mixes with $\sigma\pi$ states whose orbital components point along $y$, the lowest energy of which are expected to involve the pyrrole-type nitrogen centers bonded to hydrogen atoms. Because the $y$ spin sublevel spin–orbit couples with the more energy accessible $1n\pi^*$ states, and the $x$ spin sublevel mixes with higher energy $\sigma\pi$ singlets, we expect for these molecules that $k_y$ is greater than $k_x$.

Fig. 7. Transient triplet–triplet absorption spectra and kinetic profiles for molecules 1, 3 and 4. The spectra represent plots as a function of wavelength of the initial amplitude of the transient absorption profiles divided by the transmittance of the sample at each wavelength. The kinetic profiles show the rise and decay as a function of time of the triplet–triplet transient absorption changes excited at 590 nm (pulse repetition rate of 9.8 Hz and average energy of 8.7 mJ) and probed at (1) 440 nm for TPP, (3) 460 nm for 2-hydroxy-3-oxa-5,10,15,20-tetrakisphenylchlorin and (4) 460 nm for 2,3-dioxo-5,10,15,20-tetrakisphenylchlorin. The dashed line represents the calculated values for the best fit to a single exponential rate expression. All experiments were done at room temperature.
This is observed for all free-base porphyrin and chlorin-like molecules [49]. Furthermore, substitution of carbonyls into the conjugated ring system such as in chromophore 4 introduces additional low energy np* states that efficiently spin–orbit couple with the low-lying pp* triplet. The nonbonding electrons on the carbonyls lie in the x–y plane of the macrocycle and, from the directional arguments presented above, would be expected to enhance the decay rates of all the triplet spin sublevels. The overall effect would be a shortening of the triplet state lifetime, as is observed (Fig. 7). Indeed, molecule 4 has the shortest triplet lifetime of all the molecules described here.

The trends in the triplet lifetimes of the molecules (Table 1) are that TPC 2 has the longest lifetime, followed by TPP 1, then molecules 3 and 4, in that order. The long triplet lifetime of TPC 2 may be due to a larger energy gap between the lowest excited triplet and the ground state for this molecule compared to the others. However, because no comparative studies of the phosphorescence of TPP 1 and TPC 2 have been undertaken, it is hard to say whether this is the case. Triplet energies of 1.1–1.45 eV have been quoted in the literature for TPP [59–62]. Our computations reveal that the T1 state of TPC 2 has an energy of 0.05081 Hartree (1.383 eV) above the relaxed ground state which is higher than that of TPP 1 computed to have an energy of 0.04935 Hartree (1.343 eV). This could account for at least part of the reason why the TPC 2 lifetime is longer than that of TPP 1. More relevant for the discussion of dynamics is the difference in the triplet state and ground state energies calculated at the triplet geometry. The lack of accessible 1np* states other than on the central nitrogens explains why molecule 3 has a triplet lifetime longer than molecule 4. However, a rigorous analysis of this issue would need to include the effects of the energy gap, spin–orbit interactions and vibronic terms.

Table 1
Zero-field splitting parameters, |D| and |E|, triplet state lifetimes, τ, and EPR polarization patterns of the molecules

| Molecule | Solvent | T/K | |D|/104 cm−1 | |E|/104 cm−1 | Triplet state lifetime, τ | Polarization pattern | Reference |
|----------|--------|-----|----------------|----------------|--------------------------|----------------------|-----------|
| TPP 1    | Toluene:pyridine 10:1 (v/v) | 4.2 | 384 ± 4 | 77 ± 3 | – | aca eaa | This work |
|          | Toluene | RT | – | – | 1.15 ± 0.05 ms | – | aca eaa | This work |
|          | Toluene:pyridine 10:1 (v/v) | 4 | 387 ± 2 | 81 ± 2 | – | aca eaa | This work |
| PMMA     | Ether:ethanol | 103 | 391 ± 2a | 80 ± 1a | – | – | eaa ca– | [52] |
|          | Toluene | RT | – | – | 1.4 ± 0.3 ms | – | [69] |
| n-Octane | 4 | 363 ± 2 | 83 ± 2 | 3.3 ± 0.3 msb | – | – | [47] |
| n-Octane | 4.2 | 367 ± 4 | 90 ± 4 | – | – | [47] |
| TPC 2    | n-Octane | 4.2 | 364 ± 1 | 64 ± 1 | 4.4 ± 0.6 msb | – | [47] |
|          | Toluene:ethanol 5:1 | 77 | 364 ± 2 | 63 ± 2 | – | eae aea | [70] |
| PMMA     | n-Octane | 95 | 365 ± 9a | 62 ± 6a | – | aea eee | [52] |
|          | Toluene | 77 | – | – | 1.87 ± 0.06 ms | – | [53] |
| 3        | Toluene:pyridine 10:1 (v/v) | 4.2 | 346 ± 3 | 36 ± 2 | – | aae aee | This work |
|          | Toluene | RT | – | – | 440 ± 60 µs | – | This work |
| 4        | Toluene:pyridine 10:1 (v/v) | 4.2 | 362 ± 1 | 70 ± 1 | – | aca eae | This work |
|          | 2-MTHF | RT | – | – | 310 ± 10 µs | – | This work |

a |D| and |E| values were calculated from the spectra published by Kleibeuker et al. [52].
bDependent on light-modulation phase and frequency.
cBased on the average of the individual triplet spin sublevel decay rate constants. – means either not applicable or not determined. PMMA is polymethylmethacrylate. RT is room temperature.
3.3.2. **Triplet-state EPR spectroscopy**

Triplet-state EPR spectra can be characterized by a spin polarization intensity pattern and by static zero-field splitting (zfs) parameters. For isolated $\pi$-electron conjugated molecules, spin polarization develops from differences in the relative populating and depopulating intersystem crossing rates associated with the three spin sublevels at temperatures where thermalization of the spin populations is slowed. Fig. 8 shows polarization patterns of the EPR spectra. With the exception of the highest field transition of TPP 1, which is absorptive, molecules 1 and 4 display the same polarization pattern. The fact that the high-field line in the EPR spectrum of TPP 1 is an absorption rather than an emission most likely is due to a long triplet decay lifetime for the triplet spin sublevel $(z)$ associated with this signal. The long lifetime would allow spin–lattice relaxation to compete effectively and render the signal absorptive, even at the low temperature of 4.2 K. At higher temperatures, this high-field transition has essentially zero intensity [52]. Molecule 2 has an $aaa$ $eee$ polarization pattern, and molecule 3 has an $aae$ $aee$ polarization pattern. The different polarization patterns occur owing to changes in spin-sublevel selective spin–orbit coupling brought about by structural modifications that shift the orbital and state energies [63]. For example, forming TPC 2 from TPP 1 switches the ordering of the $b_1$ and $b_2$ orbital energies which have vastly different amounts of electron density on the central nitrogens (Fig. 5). As mentioned above, spin–orbit coupling to $1\pi\pi^*$ states involving atomic orbitals on these nitrogens is a major controlling feature in determining the rate constants for spin sublevel population and decay.

The static parameters, $|D|$ and $|E|$, represent the triplet-state dipolar interaction expressed as spatial averages of the orbital part of the triplet wavefunction.

$$|D| = \frac{3}{4} g^2 \beta^2 \left\langle \frac{r^2 - 3z^2}{r^5} \right\rangle,$$

$$|E| = \frac{3}{4} g^2 \beta^2 \left\langle \frac{y^2 - x^2}{r^5} \right\rangle,$$

where $g \approx 2.0$ is the electron $g$-value, $\beta$ is the Bohr magneton, $r$ is the interelectronic distance between the unpaired spins, and $x, y,$ and $z$ are the components of the spin angular momentum along the principal axes of the zero field splitting tensor. The magnitude of $|D|$ and $|E|$ depend on the interelectronic distance, $r$, and the symmetry of the electron distribution. For the planar $\pi$-electron conjugated molecules considered here, $\langle r^2 \rangle$ is much greater than $\langle z^2 \rangle$, and so from Eq. (2), $|D|$ is with good approximation proportional to the spatial average $\langle 1/r^3 \rangle$. Therefore, for a systematic series of increasingly larger planar $\pi$-electron conjugated molecular frameworks, $|D|$ will decrease corresponding to increasing extents of delocalization.

Changes in the symmetry of the electronic wavefunction can also affect $|D|$. Particularly important is the effect of CI. Consideration of the

![Fig. 8. Light-minus-dark difference triplet state EPR spectra taken using the conditions described in the text. The letters a and e correspond to signals in either absorption or emission. The spectrum of molecule 2 was obtained from the literature [52] and adapted for use in the figure.](image-url)
four orbital model described above predicts strong CI for the lowest excited states of D_{4h}-symmetric porphyrins and weaker CI for D_{2h}-symmetric chlorins. Fig. 5 shows the electronic distributions of the two HOMOs, \( b_1 \) and \( b_2 \), and the two LUMOs, \( c_2 \) and \( c_1 \) of the four molecules considered here. From a consideration of the magnitude of the atomic orbital coefficients represented in the figure, the effect on the magnitude of CI of the structural modifications can be understood. Saturation of a \( \beta, \beta' \)-carbon–carbon double bond in TPP to form molecules 2 or 3 leads to a destabilization of the \( c_1 \) and \( b_2 \) MOs relative to the \( c_2 \) and \( b_1 \) MOs. On the other hand, introduction of electron withdrawing carbonyl groups, as in dione 4, stabilizes the MOs that have electron density at the carbonyl positions. Both types of structural modifications will alter the extent of CI between the pairs of \( y \)-polarized, \( |c_1 b_1⟩ \) and \( |c_2 b_2⟩ \), and \( x \)-polarized, \( |c_2 b_1⟩ \) and \( |c_1 b_2⟩ \), states, because CI depends inversely on the energy differences between the interacting states. The effects of these structural alterations on the absorption spectra were discussed above. The effect of CI on the static zero-field splitting parameter, \( |D| \), may have a similar origin. If one considers only the four MOs introduced above and neglecting CI between states involving other MOs, the wavefunction for the lowest energy, \( y \)-polarized, excited triplet state can be written as

\[
\psi_T = a |b_1 c_1⟩ - (1 - a^2)^{1/2} |b_2 c_2⟩,
\]

(4)

where \( a \) is the CI coefficient characterizing the mixing between the pure \( |c_1 b_1⟩ \) and \( |c_2 b_2⟩ \) configurations [64]. Substituting Eq. (4) into (2) and following the formalisms of Kleibuker [64], we obtain

\[
|D| = a^2 D_1 + (1 - a^2) D_2 + 2a \sqrt{1 - a^2} D_{12},
\]

(5)

where \( D_1 = \langle c_1 b_1 | \hat{D} | c_1 b_1⟩ \), \( D_2 = \langle c_2 b_2 | \hat{D} | c_2 b_2⟩ \), and \( D_{12} = \langle c_1 b_1 | \hat{D} | c_2 b_2⟩ \) and \( \hat{D} \) is the spin operator in Eq. (2). Eq. (5) reveals that the magnitude of \( |D| \) is a function of \( a \) which characterizes the amount of CI.

This model predicts that the more extensive the CI, the larger will be the observed value of \( |D| \). This is born out in by the observation that the \( |D| \) value for the highly symmetric TPP 1 is the largest (\( |D| = 0.0346 \pm 0.0003 \text{ cm}^{-1} \)) and the \( |D| \) value for the least symmetric molecule 3 is the smallest (\( |D| = 0.0384 \pm 0.0004 \text{ cm}^{-1} \) of the molecules considered here. The \( |D| \) values for the remaining two molecules are very similar (see Table 1). This may be due to similar amounts of CI [64]. In any case, from the perspective of their absorption and fluorescence spectra (Fig. 4) CI appears to render TPP 1 and dione 4 porphyrin-like (narrow Soret and small \( Q \) bands), and TPC 2 and lactol 3 chlorin-like (broad Soret and larger \( Q \)-bands). However, the \( |D| \) parameter does not appear to be a sensitive probe of this interaction which would predict significantly larger values for TPP 1 and dione 4 compared to those of TPC 2 and lactol 3. This is not observed. Dione 4 has the same \( |D| \) value within experimental error as TPC 2.

To address this issue we compared the ground state and first excited triplet state geometries and charge distributions in Fig. 9. The charge distributions in the \( S_0 \) and \( T_1 \) states of these molecules are virtually identical, and the differences in the electrostatic fields are due primarily to rotation of the phenyl groups. While it is not obvious from Fig. 9, the ring system of the TPC triplet state is twisted by roughly 15° along the \( x \)-axis so that atoms in the upper left and lower right come out of the plane and atoms in the upper right and lower left go behind the plane. In contrast, the triplet state of TPP is puckered slightly so that atoms along and near to the \( x \)-axis come out of the plane and atoms at positive or negative \( y \) value go into the plane. Test calculations, however, indicate that these changes in the ring system have very little impact on the eigenvalues of the molecular orbitals near the Fermi level. Of much greater importance is the influence of the triplet manifold on the phenyl group distortion. In both molecules, Fermi correlation effects drive rotation of the phenyl groups towards planarity so that the two open shell, spin-unpaired electrons have access to the \( \pi \) system of the phenyl groups. This conformational change lowers electron–electron repulsion and provides triplet state stabilization. These results suggest that CI in the lowest excited triplet state may not be comparable to CI in the lowest excited singlet state of these molecules. Some researchers have argued that the lowest triplet states of porphyrins are essentially pure with CI excluded on the basis...
of symmetry [65,66]. Others suggest that CI among triplet states operates in parallel with that emerging between singlet states [64]. Further work on other functionalized chlorins are underway in our laboratories which will hopefully lead to a better understanding of this issue.
4. Conclusions

This work illustrates the electronic influences $\beta,\beta'$-substituents have on the spectroscopic properties of the singlet and triplet excited states chlorin-type chromophores. Our approach of studying specifically modified synthetic meso-phenylchlorin derivatives provides a set of chromophores to analyze the changes in the properties of the molecules brought about by these functionalizations. Computations using MNDO-PSCDCl methods are suitable in the modeling of these influences and provide novel insight on the spectroscopic properties of the chromophores. Future work will be directed at exploring a larger set of $\beta,\beta'$-modified chlorin-like molecules using the approach described here. The goals of this work are to explain the spectroscopic properties of chlorin-type chromophores and to develop predictive tools for the rational design of these molecules with specific optical properties.

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References