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and bacteriochlorins through chromene-annulation**

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## The limited extend of the electronic modulation of chlorins and bacteriochlorins through chromene-annulation

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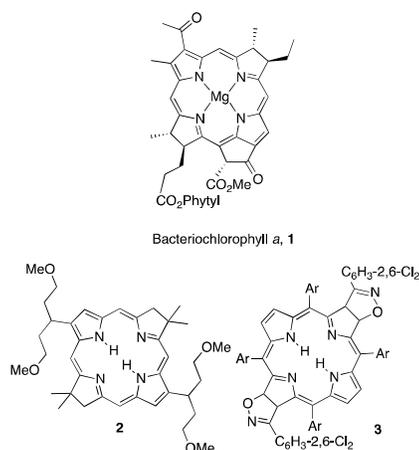
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Optical data (UV-vis absorption and fluorescence emission spectra, including fluorescence yields and lifetimes), and electrochemical measurements are used to quantify the modulation of the electronic properties of *meso*-tetrakis(pentafluorophenyl)-chlorin diol and -bacteriochlorin tetraols upon intramolecular chromene-annulation, including the investigation of regio- and stereoisomers. The small modulations of the frontier orbitals of the porphyrinoids are rationalized using DFT computations and can be traced to small electronic effects due to the co-planarized *meso*-aryl groups in combination with conformational effects.

### Introduction

Hydroporphyrins are nature's key light harvesting pigments.<sup>1</sup> Algae and higher plants utilize the green chlorin (7,8-dihydroporphyrin) magnesium(II) complexes, while the photosynthetic pigments of the anoxygenic phototropic bacteria are the purple magnesium(II) complexes of bacteriochlorins (7,8,17,18-tetrahydroporphyrins), such as BChl *a*, **1**.<sup>2</sup> Nature fine-tune their optical properties through variation of their  $\beta$ -substituents.<sup>1</sup>

The photosynthetic purple bacteria live in the water column underneath the algae. Their bacteriochlorophyll-based photosynthetic pigments make this habitat differentiation possible because they possess major absorbance bands in spectral regions, particularly in the NIR above 700 nm, where the chlorophylls absorb minimally. Since NIR light of 735 nm wavelength incidentally also possesses the deepest penetration depth in tissue,<sup>3</sup> bacteriochlorin-type chromophores have attracted significant synthetic efforts to capitalize on their NIR absorbing, emitting, and singlet oxygen sensitizing properties for use as photochemotherapeutics, imaging agents, or optical labels.<sup>4-13</sup> Their use in synthetic light-harvesting systems is also appealing.<sup>14-17</sup>



Synthetic bacteriochlorins can be prepared by total synthesis, using semi-synthetic approaches,<sup>5, 9, 18</sup> or by conversion of synthetic porphyrins.<sup>4</sup> Bacteriochlorins made by total synthesis, such as swallowtail bacteriochlorin **2**, have found multiple practical applications.<sup>10, 14, 16, 19-24</sup> The electronic modulation of the *gem*-dimethylpyrroline-based chlorins and bacteriochlorins through the variation of peripheral substituents was studied.<sup>25, 26</sup> Alternatively, the conversions of the readily available synthetic *meso*-tetraarylporphyrins<sup>27</sup> remains an attractive option for the preparation of synthetic bacteriochlorins.<sup>4</sup> Representative example is bacteriochlorin **3**, made by double-1,3-dipolar cycloaddition of a nitrile oxide to a *meso*-tetraarylporphyrin.<sup>28, 29</sup> However, once the hydroporphyrin chromophore was established, options to modulate the chromophore varies the  $\beta$ -substituents of these hydroporphyrins to fine-tune their optical properties.<sup>1</sup> Chromophore in subsequent reactions were rarely explored.<sup>26, 30</sup>

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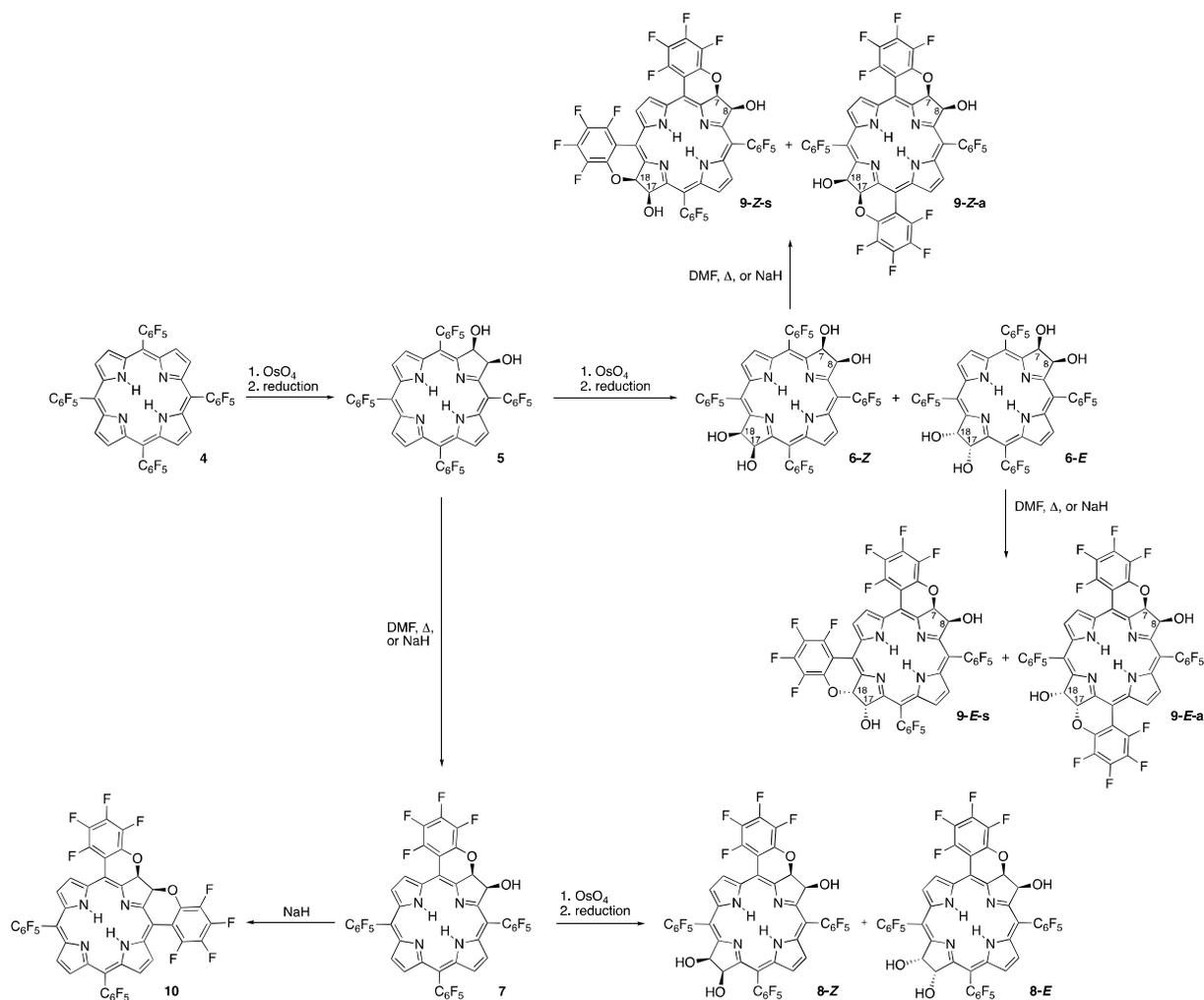
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We,<sup>31</sup> and others,<sup>32, 33</sup> described the OsO<sub>4</sub>-mediated dihydroxylation of *meso*-arylporphyrins to generate the corresponding dihydroxychlorins and tetrahydroxybacteriochlorins.<sup>34</sup> Using *meso*-C<sub>6</sub>F<sub>5</sub>-substituted porphyrin **4**, chlorin diol **5** and the two regioisomeric bacteriochlorins **6-Z** and **6-E** were thus formed

(Scheme 1).<sup>31, 35</sup> The two bacteriochlorins are differentiated by the relative orientation of the two *cis-vic*-diol functionalities that may be facing the same side defined by the idealized planar macrocycle (**6-Z**), or opposing sides (**6-E**).



**Scheme 1.** Syntheses of chlorindiol **5** and bacteriochlorintetraols **6-Z** and **6-E** by OsO<sub>4</sub>-mediated dihydroxylation of porphyrin **4**,<sup>31</sup> and generation of mono-chromene-annulated chlorin **7**<sup>35</sup> and stereoisomeric bacteriochlorins **8-Z** and **8-E**, and the regioisomeric bis-chromene-annulated bacteriochlorins **9**.<sup>35</sup>

We also described a way to modify *meso*-C<sub>6</sub>F<sub>5</sub>-substituted dihydroxychlorin **5** and the two bacteriochlorins **6-Z** and **6-E** using intramolecular S<sub>N</sub>Ar displacements of an *o*-F of the *meso*-C<sub>6</sub>F<sub>5</sub> groups by the neighboring alcohols, forming chromene-annulated chlorin **7** or chromene-annulated bacteriochlorins **8-Z** and **8-E**, respectively (Scheme 1).<sup>35, 36</sup> Related S<sub>N</sub>Ar reactions of *meso*-C<sub>6</sub>F<sub>5</sub>-substituted porphyrinoids are known.<sup>37, 38</sup> The tetrahydroxybacteriochlorins can, in theory, form a chromene-annulated linkage with each of the two sets of diol moieties, giving rise to four isomeric products of the bis-linked bacteriochlorin **9**, depending on whether the bacteriochlorin isomers **6-E**- or **6-Z** were the starting materials, and whether the two opposing aryl groups rotated in the same absolute

direction around the macrocycle-*meso-ipo*-phenyl bond, or in opposite directions to form the ether linkage. The former option leads to the formation of two ring closures on diagonally opposed 7,17-positions of the macrocycle, forming the *-a* (*anti*) isomer, while the latter option leads to the formation of the fused rings on the 7,18-positions on same side of the macrocycle, forming the *-s* (*syn*) isomer (Scheme 2).<sup>36</sup> Interestingly, the **9-E-s** isomer was experimentally not observed to form, a finding that was rationalized by conformational effects.<sup>36</sup> We also begun to study the oxidative transformations of the chromene-annulated chlorins.<sup>39</sup>

Most *meso*-tetraarylporphyrins in which a (short) covalent linkage between a  $\beta$ -position and the adjacent *meso*-aryl group was established exhibit bathochromically shifted optical spectra compared to their parent compounds; this was rationalized by the presumed extension of the macrocyclic  $\pi$ -system through co-planarization of the annulated *meso*-aryl group.<sup>40-43</sup> In addition, a deformation of the macrocycle planarity generally tends to cause red-shifted optical spectra.<sup>44, 45</sup> As a result of the annulation, we previously computed the chromene-annulated chromophores to be slightly non-planar.<sup>35, 36</sup> In light of these two factors that can reasonably be expected to be additive,<sup>46</sup> it is somewhat surprising that the actual bathochromic shifts observed for the chromene-annulated systems were relatively modest (8-30 nm shift per annulation).

At the time of the discovery of the chromene-annulated hydroporphyrins, the details of the origins of their electronic modulations were not further investigated.<sup>35, 36</sup> This study fills this gap and illuminates the changes of the electronic structures of the *meso*-C<sub>6</sub>F<sub>5</sub>-substituted chlorins and bacteriochlorins upon chromene-annulation, including a comparison of the various regio- and stereo-isomers, using optical, electrochemical, and computational data. We thus contribute to the further understanding of the class of synthetic *meso*-aryl-substituted bacteriochlorins and the scopes and limits of the degree to which their electronic structures can be tuned by chromene-annulation.

## Results and discussion

### DFT Calculations

The DFT-computed electronic structures of the chlorins and bacteriochlorins under investigation confirmed, on one hand, the well-known trends that distinguish the frontier orbitals of chlorins and bacteriochlorins and, on the other hand, provided insight into the subtle effects of the chromene-annulation (Figures 1, Table 1). As generally observed for bacteriochlorins compared to chlorins,<sup>47</sup> and reflected in the differing UV-vis spectra of these two hydroporphyrin classes (Figure 3, Table 2; discussed in detail below), their HOMO-LUMO gap is narrowed because of a significant lowering of the LUMO and a minor lifting of the HOMO, whereas the LUMO+1 is significantly lifted (giving rise to the generally blue-shifted Soret band of the bacteriochlorins).<sup>47</sup> The experimentally obtained HOMO-LUMO energy gaps are comparable to the literature data (1.35-1.45 eV for the bacteriochlorins and 1.72-1.98 eV for the chlorins),<sup>48-50</sup> indicating that the HOMO-LUMO energy gap of the hydroporphyrins is not much affected by the presence of the *meso*-pentafluorophenyl groups. However the absolute position of the frontier orbitals is somewhat lowered, as also observed for the parent porphyrins.<sup>51</sup> The increasing number of chromene-annulations leads to successive destabilization of the HOMO as well as stabilization of the LUMOs (as seen, e.g., in the series **5**  $\rightarrow$  **7**  $\rightarrow$  **10**). The frontier orbital levels of the comparable regioisomeric *E*- and *Z*-series (e.g. **9-E-s** vs. **9-Z-s**) are essentially identical, but the isomers within each series

(e.g. **9-E-s** vs. **9-E-a**) differ slightly on account of their slightly differing conformations.<sup>36</sup> Overall, the DFT calculations faithfully reproduce the experimental electrochemical data and trends observed by UV-vis spectroscopy, presented in detail below.

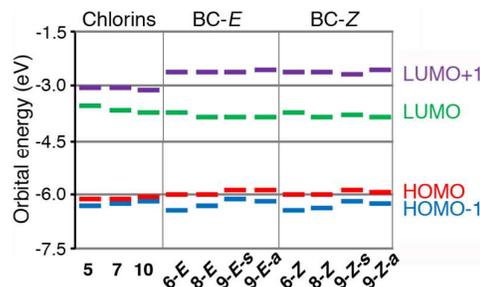


Figure 1. Graphical representation of the frontier energy levels of the hydroporphyrins calculated; see also Table 1 and ESI.

Table 1. Computed HOMO and LUMO energies (in eV) as per DFT.

Compound <sup>a</sup>	HOMO-1	HOMO	LUMO	LUMO+1	HOMO-LUMO gap
C diol <b>5</b>	-6.36	-6.17	-3.56	-3.06	2.61
Mono-fused C diol <b>7</b>	-6.28	-6.17	-3.66	-3.07	2.51
Bis-fused C diol <b>10</b>	-6.21	-6.11	-3.72	-3.14	2.39
BC tetraol <b>6-Z</b>	-6.46	-6.01	-3.74	-2.62	2.26
BC tetraol <b>6-E</b>	-6.46	-6.01	-3.75	-2.62	2.26
Mono-fused BC <b>8-Z</b>	-6.37	-6.00	-3.85	-2.63	2.15
Mono-fused BC <b>8-E</b>	-6.35	-6.01	-3.84	-2.64	2.17
Bis-fused BC <b>9-Z-s</b>	-6.24	-5.94	-3.85	-2.58	2.09
Bis-fused BC <b>9-E-s</b>	-6.23	-5.93	-3.86	-2.59	2.08
Bis-fused BC <b>9-Z-a</b>	-6.20	-5.91	-3.82	-2.68	2.09

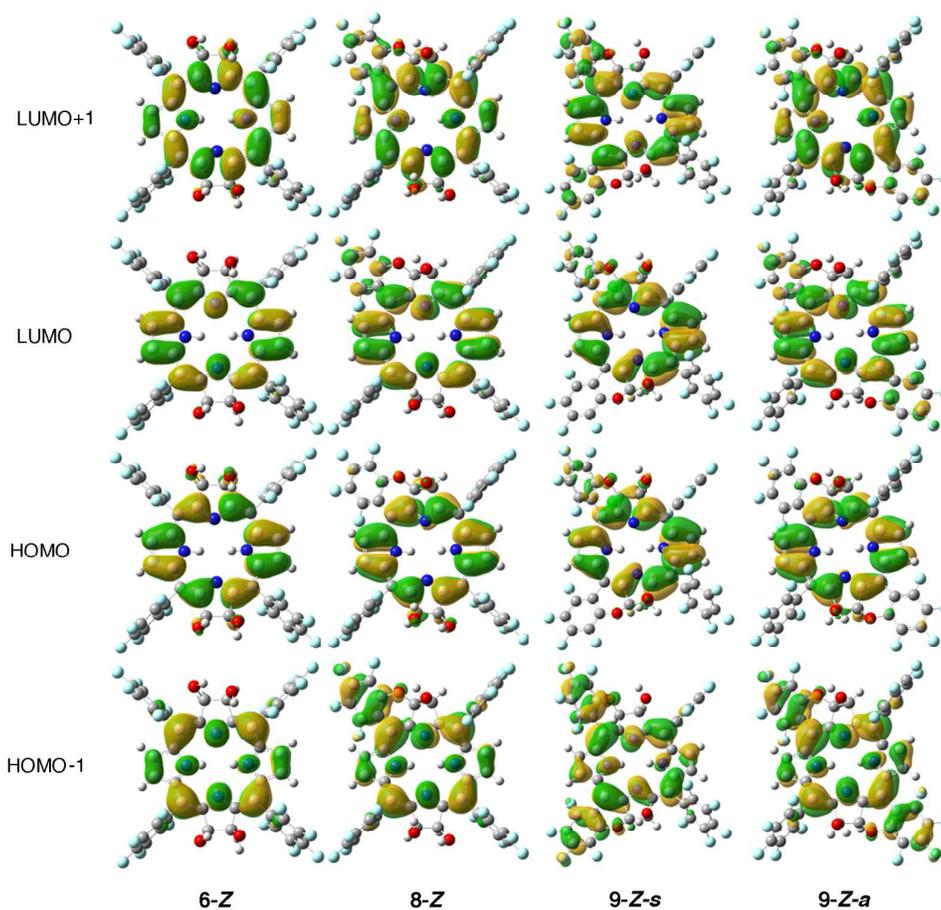
<sup>a</sup> C = chlorin, BC = bacteriochlorin

Considering the frontier orbitals in detail (Figure 2, see also ESI), the principal symmetry of the MOs is not affected by the annulation. In fact, the orbitals centered on the *meso*-aryl group 'co-planarized' by chromene-annulation (there are still dihedral angles between 20 and 40° observed between the mean plane of the porphyrinic chromophore and the aryl group) contribute only to a minor degree to the frontier orbitals, and if so, particularly those primarily responsible for the UV-vis spectrum of the hydroporphyrins (HOMO, LUMO, LUMO+1). As a consequence, the UV-vis spectra of the chromene-annulated hydroporphyrins are predicted to very much retain the spectral features of their parent compounds, as is indeed the case (Figure 3).



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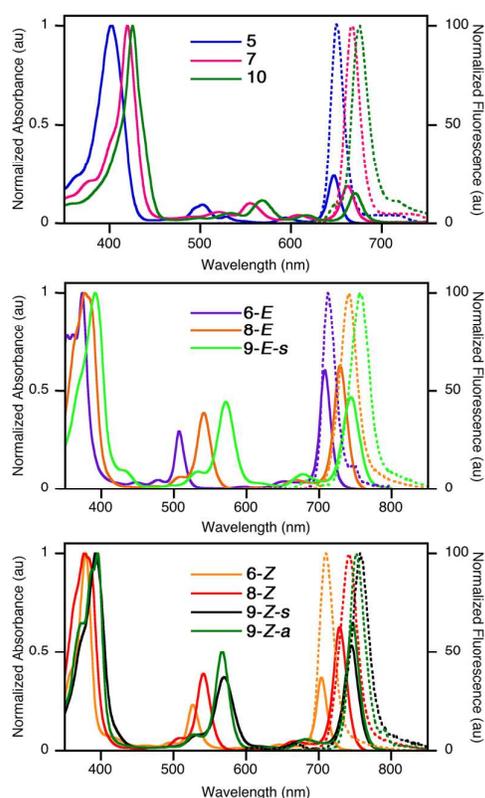


**Figure 2.** Representation of the frontier orbitals of the bacteriochlorin series 6-Z, 8-Z, 9-Z-s, and 9-Z-a displayed at an isosurface value of 0.02 a.u.; see also Table 1, Figure 1, and ESI.

### UV-vis spectra

The general appearance of the UV-vis absorption spectra of the chromene-annulated hydroporphyrins clearly reflect their nature as chlorins or bacteriochlorins (Figure 3, Table 2).<sup>35, 36</sup> The effects of the chromene-annulation are clearly visible within each class of hydroporphyrins: Chlorins of type **7** or **10** are characterized by red-shifted optical spectra when compared to the non-annulated starting materials (16 nm for the conversion of chlorin **5** to mono-fused **7** and an additional 8 nm for the second fusion in **10**). The calculated and electrochemically determined frontier orbital levels suggests that these bathochromic shifts are primarily because of

lowered LUMO level energies, a likely effect of the increased—albeit minor— $\pi$ -overlap between the *meso*-phenyl and porphyrinic chromophore, due to greater co-planarity through annulation.



**Figure 3.** Overlay of the UV-vis absorption and normalized fluorescence emission spectra ( $\text{CH}_2\text{Cl}_2$ ,  $25^\circ\text{C}$ ) of the hydroporphyrins indicated;  $\lambda_{\text{excitation}} = \lambda_{\text{Soret}}$ .

The optically observed red-shifts among the bacteriochlorin series upon chromene-annulation are larger than in the chlorin series (mono-fused bacteriochlorin **8-Z** shows a  $\sim 13$  nm red-shift compared to the parent bacteriochlorin **6-Z**, while double chromene-annulation leads to a 29/32 nm red-shift for **9-Z-s**/**9-Z-a**). This is likely because hydroporphyrinoid flexibility increases with increasing degree of saturation.<sup>52</sup> Thus bacteriochlorins are susceptible to larger deformations upon annulation, and these deformations tend to lift the HOMO levels (cf. to Figure 1, Table 1).<sup>44, 45</sup> In addition to the lowered LUMO levels this results in a larger red-shift per annulation in the bacteriochlorins compared to the chlorins. Small but clearly distinguishable differences seen between the absolute positions of the frontier orbitals in the two regioisomers are interpreted to be the result of their differing conformations.<sup>36</sup>

**Table 2.** Optical parameters ( $\text{CH}_2\text{Cl}_2$  at ambient T) of the compounds investigated.

Compound <sup>a</sup>	UV-vis Absorption Spectrum $\lambda_{\text{max}}$ ( $Q_y(0,0)$ )/nm ( $\log \epsilon$ )	Fluorescence Emission $\lambda_{\text{max}}$ /nm ( $\lambda_{\text{excitation}} = \lambda_{\text{Soret}}$ )	Q-state energy <sup>c</sup> (eV)	Fluorescence Emission Quantum Yield ( $\phi$ )	Fluorescence Lifetime $\pm 10\%$ (ns)
P <b>4</b> <sup>b</sup>	654 (2.63)	657	1.89	0.13	9.3
C diol <b>5</b>	647 (4.63)	649	1.91	0.34	6.9
Mono-fused C diol <b>7</b>	663 (4.70)	668	1.89	0.17	3.1
Bis-fused C diol <b>10</b>	671 (4.50)	676	1.84	0.20	3.6
BC tetraol <b>6-Z</b>	708 (4.74)	712	1.75	0.01	4.0
BC tetraol <b>6-E</b>	716 (4.32)	728	1.72	0.01	3.2
Mono-fused BC <b>8-Z</b>	729 (5.02)	740	1.69	0.06	3.0
Mono-fused BC <b>8-E</b>	729 (5.05)	740	1.69	0.06	3.3
Bis-fused BC <b>9-Z-s</b>	745 (5.05)	760	1.65	0.05	3.6
Bis-fused BC <b>9-E-s</b>	746 (4.98)	761	1.65	0.03	2.7
Bis-fused BC <b>9-Z-a</b>	748 (5.06)	759	1.65	0.06	2.9

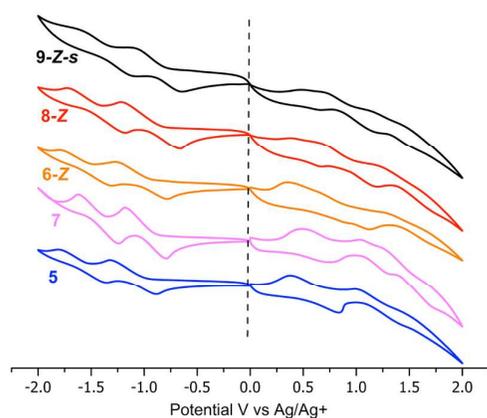
<sup>a</sup> P = porphyrin, C = chlorin, BC = bacteriochlorin <sup>b</sup> From ref. 51. <sup>c</sup> Average energy of the  $Q_y(0,0)$  absorption and fluorescence bands

### Electrochemistry

Cyclic voltammograms for all compounds were recorded (Figure 4, Table 3) and relative HOMO–LUMO band gap energies were calculated based on the electrochemical data. Here we must be careful to distinguish between the electrochemical and optical HOMO–LUMO energy gaps. The optically measured energy gap is the energy difference between a molecule with  $N$  electrons in its ground state and the same  $N$ -electron molecule in its excited state. In contrast, while the electrochemical oxidation potential can be taken as giving the most realistic energy level of the HOMO state, the reduction potential gives the energy of an  $(N+1)$ -electron ionized molecule, which is not the same as the  $N$ -electron molecule's LUMO state, since that state will have shifted upward in energy owing to the negative charge.<sup>53, 54</sup> In principle, the computed HOMO–LUMO energy gap should approximate the optical Q-state energy. In our results, we find that the optical and electrochemical HOMO–LUMO gaps are fairly close to each other (generally within 0.2 eV), while the computed HOMO–LUMO gap was over-estimated by 0.5–0.9 eV (compare data in Tables 1, 2 and 3, graphical representation of the trends of the values in ESI). This is not surprising due to the many approximations used in DFT. The computed trends of the

HOMO-LUMO gaps are reflected in the optically and electrochemically determined values.

Except for bacteriochlorin tetraol **6-E** and bis-linked bacteriochlorin **9-Z-a**, all compounds undergo two reversible reductions forming stable radical anions and dianions. The bacteriochlorins **6-E** and **9-Z-a** show only quasi-reversible or fully irreversible reductions; these compounds are thus omitted from detailed discussion. We previously observed the surprisingly distinct chemical reactivity and conformations of the two bacteriochlorin tetraol isomers **6-E** and **6-Z**.<sup>31</sup> For chlorins **5**, **7**, and **8-E**, the first oxidation couples are reversible, however other compounds only show ill-resolved quasi-reversible or irreversible oxidations, a common observation for free-base porphyrins and hydroporphyrins.<sup>55</sup> The derived general lower LUMO and higher HOMO levels of the bacteriochlorins compared to the chlorins are as expected based on the nature of the hydroporphyrins.<sup>47</sup> Thus, chromene-annulation also does not change the native electrochemical characteristics of the parent hydroporphyrins.



**Figure 4.** Representative cyclic voltammograms of the compounds indicated (dry  $\text{CH}_2\text{Cl}_2$ , 0.1 M TBAPF<sub>6</sub>, [X]  $\sim 10^{-3}$  M, scan rate of 200 mV/s).

**Table 3.** Electrochemical half-wave potentials of the compounds investigated

Compound <sup>a</sup>	Reduction		Oxidation		HOMO-LUMO gap
	$E_{red2}^{1/2}$	$E_{red1}^{1/2}$	$E_{ox1}^{1/2}$	$E_{ox2}^{1/2}$	
C diol <b>5</b>	-3.48	-3.94	-5.67	-6.26	1.73
Mono-fused C diol <b>7</b>	-3.63	-4.07	-5.69	-6.24	1.62
Bis-fused C diol <b>10</b>	-3.50	-3.88	(-5.60) <sup>c</sup>	(-6.10) <sup>c</sup>	(1.72) <sup>c</sup>
BC tetraol <b>6-Z</b>	-3.51	-4.06	-5.68	-5.97	1.62
BC tetraol <b>6-E</b>	(-3.75) <sup>c</sup>	(-4.15) <sup>c</sup>	(-5.84) <sup>c</sup>	(-5.92) <sup>c</sup>	(1.69) <sup>c</sup>
Mono-fused BC <b>8-Z</b>	-3.61	-4.12	-5.59	-6.00	1.47
Mono-fused BC <b>8-E</b>	-3.64	-4.15	-5.68	-6.20	1.53
Bis-fused BC <b>9-Z-s</b>	-3.72	-4.20	-5.64	-6.02	1.44
Bis-fused BC <b>9-E-s</b>	-3.73	-4.21	-5.66	-6.00	1.45
Bis-fused BC <b>9-Z-a</b>	-	-3.83	-5.40	-	1.57

<sup>a</sup> C = chlorin, BC = bacteriochlorin

<sup>b</sup> Measured reduction and oxidation potentials were referenced to Fc/Fc<sup>+</sup>, converted using  $E_{Fc/Fc^+} = +0.63\text{V}$  vs NHE, then converted to eV using a vacuum level potential of  $-4.44\text{V}$  vs NHE, for ease of comparison with computed energy levels. For a table of the data in V vs. NHE see ESI.

<sup>c</sup> Unreliable data based on irreversible, ill-defined peaks.

## Fluorescence

The fluorescence emission wavelengths track the  $\lambda_{\text{max}}$  values of the absorption spectra (Figure 5, Table 2), all with the small Stokes shift typical for porphyrinoids. The fluorescence emission quantum yield is generally lower for bacteriochlorins than for chlorins,<sup>4</sup> and this is also observed here. What surprised us were the two opposing trends seen in the fluorescence quantum yields upon annulation within each class of hydroporphyrins. Chromene annulation cuts the fluorescence quantum yield in half when considering the quantum yields for the parent chlorin **5** and its mono-annulated derivative **7**. In contrast, the (overall much lower) quantum yield for the mono-annulated bacteriochlorin (**8-Z** or **8-E**) significantly improved over that of the parent chromophore (**6-Z** or **6-E**, respectively). The trends are not additive, as the bis-annulated chromophores possess essentially the same fluorescence quantum yields as their mono-annulated analogues.

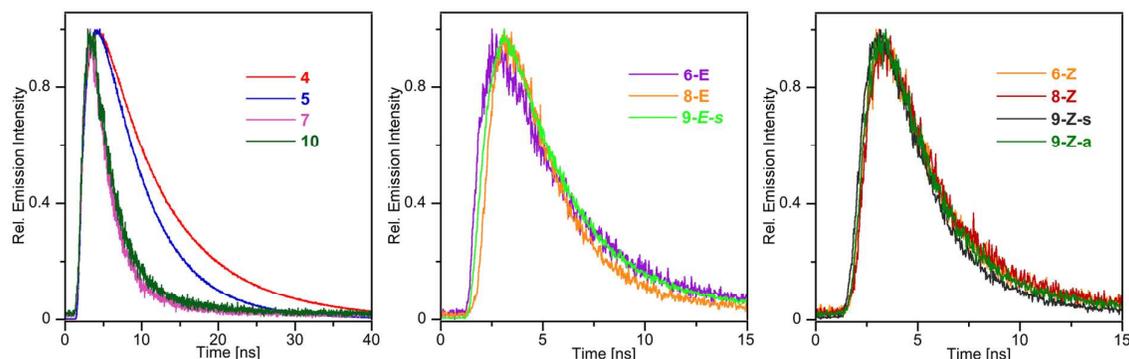


Figure 5. Overlay of the time-dependent fluorescence emission traces ( $\text{CH}_2\text{Cl}_2$ ,  $25^\circ\text{C}$ ) of the compounds indicated.

The fluorescence lifetimes of the parent porphyrin are relatively long (Figure 5, Table 3), and those of the corresponding chlorin are shorter. Comparing this with literature data, this trend is not always observed.<sup>56</sup> Chromene annulation shortens the fluorescence lifetime (by 50% in the chlorin case, 25% or less in the already much shorter lifetimes in the bacteriochlorin series), again with the effect not being additive.

When we set out with the work, we had hypothesized that the assumed rigidification of the macrocycle through chromene annulation might increase the fluorescence quantum yields and extend the fluorescence lifetimes. The fact that this hypothesis is not supported by the findings suggests that either electronic effects associated with the chromene oxygens or conformational effects may override the surmised effects of greater conformational rigidity.

## Experimental

### Materials

All chlorins and bacteriochlorins were prepared as reported in the literature (Scheme 1).<sup>31, 35, 36</sup>

### Optical Spectra

The optical data of all chromophores compared were recorded in  $\text{CH}_2\text{Cl}_2$  at ambient temperature on a Cary 50 UV-vis absorption spectrophotometer or Cary Eclipse fluorescence spectrophotometer. Fluorescence yields: The fluorescence yields ( $\phi$ ) were determined relative to those of *meso*-tetraphenylporphyrin ( $\phi = 0.11$  in benzene,<sup>57</sup> calculated to be 0.09 in  $\text{CH}_2\text{Cl}_2$ );  $\lambda_{\text{excitation}} = \lambda_{\text{Soret}}$ .

### Time-resolved photoluminescence measurements

To measure the fluorescence lifetime of the porphyrin **4** and the hydroporphyrins ( $\text{CH}_2\text{Cl}_2$ ,  $\sim 10^{-6}$  M, ambient conditions), the samples were excited with a pulsed laser at 405 nm (PicoQuant,  $\sim 30$ – $40$  ps pulse duration, 2.5 MHz repetition rate). The photoluminescence of the solutions was focused onto a single-photon detector ( $\tau$ -SPAD, PicoQuant) that was equipped with the appropriate spectral filter. The photoluminescence decays were acquired using a time dependent single photon counting module (PicoHarp 300, PicoQuant) with a time resolution set at 32 ps. The decay curves were then fitted to a single exponential function using Origin Pro software to determine the lifetime values.

### Electrochemistry

The CV measurements of all the porphyrins were recorded on a CHI 600D electrochemical analyzer, with a standard three-electrode cell assembly. The supporting electrolyte was 0.1 M tetrabutylammonium hexafluorophosphate ( $\text{TBAPF}_6$ ) dissolved in dry  $\text{CH}_2\text{Cl}_2$ . Platinum wires served as working and counter electrodes. An  $\text{Ag}/\text{Ag}^+$  couple was used as the reference electrode and ferrocene was used as an internal reference. All porphyrins were measured at a concentration of  $\sim 1$  mM and at a scan rate of 200 mV/s. Prior to scanning, the solutions were sparged with purified  $\text{N}_2$  for 5 min.

### Computations

The geometries of all chlorin and bacteriochlorin structures were optimized using the Becke, three parameter, Lee-Yang-Parr (B3LYP) hybrid density functional<sup>58, 59</sup>, a 6-31+g(d,p) basis set, and an ultrafine integration grid, as implemented in Gaussian 09 Revision D.01.<sup>60</sup> This model chemistry has been used previously to examine some of these,<sup>36</sup> or related,<sup>46</sup>

compounds. A vibrational analysis was performed for each structure and confirmed the absence of imaginary frequencies.

## Conclusions

Chromene-annulation within *meso*-tetrakis(pentafluorophenyl)-chlorins diol and -bacteriochlorin tetraols are a viable way to modulate their optical properties in small increments. Optical data (UV-vis absorption and fluorescence spectra, including quantum yields and lifetimes), electrochemical measurements, and DFT calculations illuminate some factors behind the (limited) extent of the modulation: Chromene-annulation does not change the general characteristics of the parent chromophore, but the absolute magnitude of the modulation is significantly smaller than that observed in a number of other annulated porphyrinoids.<sup>40-43, 61, 62</sup> We posit that, in a most simplistic sense, the more co-planar *meso*-aryl groups in the annulated systems are responsible for the lowering of the LUMO level while the conformational distortions caused by the annulations slightly elevate the HOMO levels, with the sum of the small effects causing the bathochromically shifted spectra. The overall electronic effect of the annulation is small, however. The state of reduction of the macrocycle has a much larger effect on their electronic structure than any of the modulations caused by the annulation reactions, but this is not necessarily always the case in the field of annulated porphyrinoids.<sup>61, 62</sup> The optically determined HOMO-LUMO gap suggest that effects of the rigidification of the macrocycle through annulation may be mitigated by the chromophore non-planarity effects also caused by the annulation reaction.

Thus, while questions still remain, this work adds more in-depth understanding of the effects of annulation to (hydro)porphyrins involving the *meso*-aryl groups, a rapidly expanding group of compounds.

## Conflicts of interest

There are no conflicts to declare.

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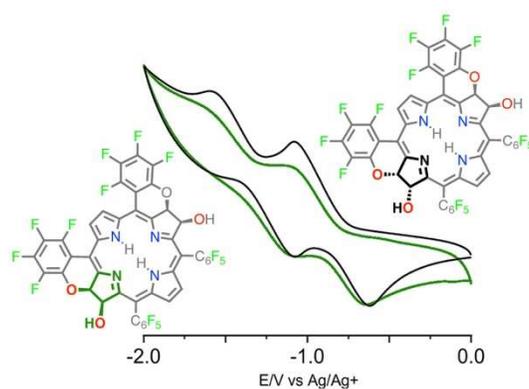
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**The limited electronic modulation of chlorins and bacteriochlorins  
through chromene-annulation**

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Optical data and electrochemical measurements quantify the modulation of the electronic properties of *meso*-C<sub>6</sub>F<sub>5</sub>-modified chlorins and bacteriochlorins upon intramolecular chromene-annulation.