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meso-Tetrakis(pentafluorophenyl)porphyrin-Derived Chromene-Annulated Chlorins

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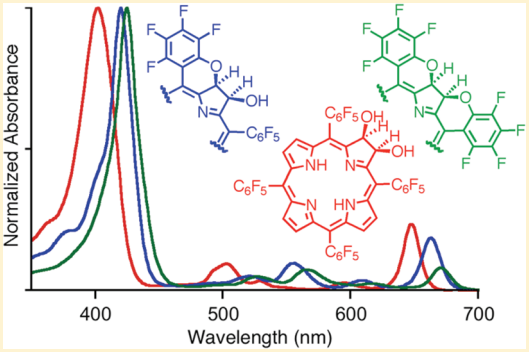
Supporting Information

ABSTRACT: The synthesis of mono- and bis-chromene-annulated *meso*-(pentafluorophenyl)chlorins from *meso*-tetrakis(pentafluorophenyl)-porphyrins by an OsO_4-mediated dihydroxylation reaction, followed by an intramolecular nucleophilic aromatic substitution reaction, is described. The reaction sequence is applicable to the free base systems as well as their Zn(II), Ni(II), Pd(II), and Pt(II) complexes. The optical properties (UV–vis and fluorescence spectra) of the (metallo)chlorin-like chromophores that possess slightly red-shifted optical spectra compared to the corresponding 2,3-dihydroxychlorins are reported. Molecular modeling and ^{1}H–^{19}F-HOESY NMR spectroscopy provide indications for the conformation of the chromene-annulated chromophores. Using ^{1}H–^{1}H COSY and ^{19}F–^{19}F QF-COSY NMR spectra, we interpret the ^{1}H and ^{19}F NMR spectra of the porphyrins and chlorins, thus providing a refined reference point for the use of ^{19}F NMR spectroscopy as a diagnostic tool in the analysis of *meso*-pentafluorophenyl-substituted porphyrinoids.



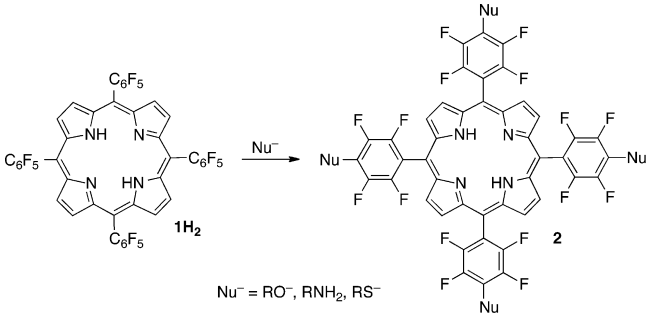
INTRODUCTION

meso-Tetraarylporphyrins are the most commonly used synthetic porphyrins.[1] Their popularity arises primarily from their straightforward syntheses and the availability of a wide variety of aryl-functionalized derivatives.[2] Most aryl derivatives do not affect the electronic properties of the porphyrinic chromophore in any major way.[3] However, the total of 20 strongly electron-withdrawing fluorine atoms in *meso*-tetrakis-(pentafluorophenyl)porphyrin (**1H$_2$**) have a significant inductive effect on the chromophore. Thus, the chemical and physical properties of **1H$_2$** are altered when compared to those of the parent phenyl-substituted systems.[4,5]

Another consequence of the *meso*-pentafluorophenyl substitution, the electron-poor porphyrin **1H$_2$** shows distinct and high reactivity with a number of reagents,[6,7] and it is considered to be oxidatively more robust than its phenyl analogue.[8] Moreover, the solubility of porphyrin **1H$_2$** and its neutral metal complexes is significantly better in common organic solvents than that of *meso*-tetrakisphenylporphyrin or many of its simple phenyl derivatives (such as 4-methyl, 4-methoxy-, or 4-carboxyphenyl derivatives).

Many expanded porphyrins, porphyrin isomers, and porphyrin analogues were prepared carrying pentafluorophenyl groups.[9,10] The pentafluorophenyl group is not chemically inert. It has been known for some time that porphyrin **1H$_2$** readily undergoes a nucleophilic aromatic substitution reaction (S_NAr) with a range of nucleophiles (Scheme 1).[10−15] These reactions led, inter alia, to the formation of a number of porphyrin–sugar hybrids (of type **2**).[12] This type of aryl substitution is not limited to pentafluorophenyl-derivatized porphyrinoids.[10,16]

Scheme 1. S_NAr Reaction of the *p*-Fluoro Atom in Tetrakis(pentafluorophenyl)porphyrin 1H$_2$



The modulation of the porphyrinic chromophore, such as affecting a red-shift and increase of the absorptivity of the longest wavelength of absorbance band (λ_{max}), is desirable for a number of applications.[17] A classic technique to accomplish this shift is the conversion of porphyrins to chlorins,[18] such as the conversion of tetraphenylporphyrin to the corresponding 2,3-dihydroxychlorin **3^{Ph}H$_2$**.[19−21]

We also demonstrated that the formal insertion of an oxygen atom between the pyrrolidine β,β'-carbons of **3^{Ph}H$_2$** generates further red-shifted morpholinochlorins.[20,22,23] Additionally, the electronic structures of these chromophores can be modulated by the establishment of a β-to-*o*-linkage, such as in **4**.[23−29] The origin of the electronic modulation of the porphyrinic

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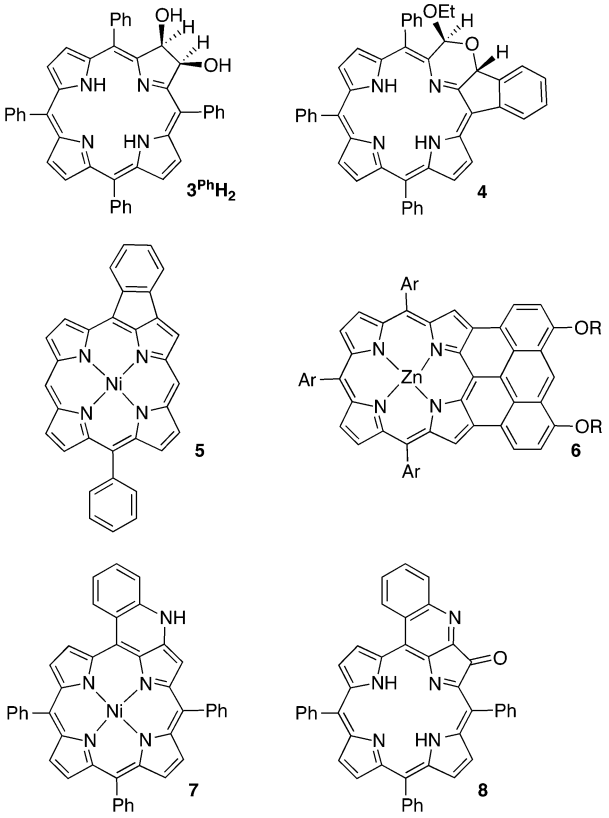

chromophore upon establishment of a β-to-o-linkage is that this linkage forces the *meso*-phenyl group into greater coplanarity with the porphyrinic chromophore.[25] This is well described and was utilized by a number of groups to synthesize annulated porphyrins containing β-to-o-aryl linkages, ranging from the minimalist compound **5** described by Boyle and co-workers,[26] incorporating a five-membered ring between phenyl group and porphyrin ring, to the anthracenyl-annulated system **6** introduced by Anderson and co-workers,[27] forming two six-membered rings. Heteroatoms were also used as linkers. For instance, Callot described the use of an sp^3-nitrogen linking the β-position and the adjacent phenyl group, **7**,[28] and we recently reported the sp^2-nitrogen-linked quinoline-annulated porphyrin **8**.[29]

The pentafluorophenyl groups have multiple implications on the ability to study the porphyrinoids by NMR spectroscopy. On one hand, the ^{1}H NMR spectra of pentafluorophenyl-substituted porphyrinoids are, naturally, greatly simplified when compared to those of the nonfluorinated analogues. On the other hand, ^{19}F–^{13}C couplings in regular $\{^1$H$\}$ ^{13}C NMR spectra complicate the interpretation of their ^{13}C NMR spectra. The ^{19}F nucleus (100% isotopic abundance) is an I = 1/2 nucleus of high magnetogyric ratio.[30] Thus, the ^{19}F NMR spectra can be also used as a diagnostic tool in pentafluorophenyl-substituted porphyrinoids, but a literature survey shows that the ^{19}F NMR spectra of compounds of lower symmetry are either not reported, or when reported, are commonly not assigned.[7,13,14,31]

We report here an intramolecular reaction between an oxygen atom of a 2,3-dihydroxypyrrolidine moiety in *meso*-tetrakis(pentafluorophenyl)-2,3-dihydroxychlorin and the *o*-position of the flanking pentafluorophenyl group to generate novel chromene-annulated chlorins. This is the first report in which an intramolecular reaction toward the synthesis of annulated porphyrinoids takes advantage of the particular *o*-fluorine reactivity of the *meso*-pentafluorophenyl group. Next to the optical spectra of the free base chromophores and their Zn(II), Ni(II), Pd(II), and Pt(II) complexes, we will also provide ^{19}F NMR spectra of a range of chlorins that were nearly fully assigned using ^{19}F–^{19}F COSY and ^{1}H–^{19}F HOESY NMR spectra, thus filling a diagnostic gap.

RESULTS AND DISCUSSION

Synthesis of *meso*-Tetrakis(pentafluorophenyl)-2,3-dihydroxychlorins 3. The preparation of tetraaryl-2,3-dihydroxychlorins via the OsO_4-mediated dihydroxylation of the corresponding porphyrin is well described.[19−21] This process is a two-step sequence: first, the formation of the osmate ester and, second, the reduction of the osmate ester using H_2S. Using *meso*-pentafluorophenylporphyrin $\mathbf{1H_2}$ as a substrate, the osmylation is rapid and high yielding, likely a consequence of its high solubility.[32] Alas, the osmate ester reduction step using H_2S failed to cleanly produce the desired 2,3-dihydroxychlorin $\mathbf{3H_2}$ as H_2S also induces undesirable S_NAr reactions at the aryl *p*-positions. Thus, we screened a number of other potential reductants/chelators (elemental sulfur powder, sodium dithionite, *o*-phenylene diamine) and found stirring a $CHCl_3$/pyridine solution of the osmate ester with a saturated solution of sodium bisulfite in 1:1 mixture of H_2O and MeOH to deliver the best results.[33,34] Thus, *meso*-tetrakis(pentafluorophenyl)-2,3-dihydroxychlorin $\mathbf{3H_2}$ became available in 65−70% isolated yields (at a 500 mg scale) (Scheme 2).

The reaction sequence described for the synthesis of free base diol $\mathbf{3H_2}$ is also applicable to the dihydroxylation of the Zn(II), Ni(II), Pd(II), and Pt(II) complexes of $\mathbf{3H_2}$. The mild conditions required to insert Zn(II) into diol $\mathbf{3H_2}$ allow the facile preparation of **9Zn**, but **9Ni**, **9Pd**, and **9Pt** can only be prepared via the dihydroxylation of the corresponding metalloporphyrins. Attempts to metalate diol $\mathbf{3H_2}$ under standard conditions (DMF or benzonitrile, heat) resulted in the degradation of the diol.[35,36]

Chlorin diol $\mathbf{3H_2}$ and its metal complexes possessed the expected spectroscopic and analytical properties. This chlorin is used as the benchmark compound against which we compare the novel chromene-annulated chlorins. For a comparative discussion of the ^{1}H and ^{19}F NMR, UV−vis, and fluorescence emission spectra of $\mathbf{3H_2}$, see below.

Synthesis of Chromene-Annulated Chlorins. Refluxing a solution of dihydroxychlorin $\mathbf{3H_2}$ in DMF (or using a strong base, see below) converts the greenish brown starting material over the course of 45 min in high yield to a less polar, purple product, $\mathbf{9H_2}$ (Scheme 2). The dihydroxychlorin metal complexes **3M** (M = Zn(II), Ni(II), Pd(II), Pt(II)) also formed the corresponding metallochlorin complexes, **9M**. This indicated that the reaction was independent of the presence of the central metal and the metal-induced changes of electronics, conformation, and conformational flexibility.

The free base compound $\mathbf{9H_2}$ possesses a typical chlorin-type UV−vis spectrum that is slightly red-shifted compared to the starting chlorin diol $\mathbf{3H_2}$. Analogously, the metal complexes **9M** are characterized by regular and slightly red-shifted metallochlorin spectra. See below for a detailed description of their optical spectra.

The composition of the products $\mathbf{9H_2}$/**9M**, as determined by HR-MS (ESI+, 100% CH_3CN), indicated that a loss of a single HF had taken place in the conversion from the starting materials $\mathbf{3H_2}$/**3M**. We, and others, previously showed that, under the conditions of collision-induced mass spectrometry (particularly under ESI− conditions), pentafluorophenyl-substituted

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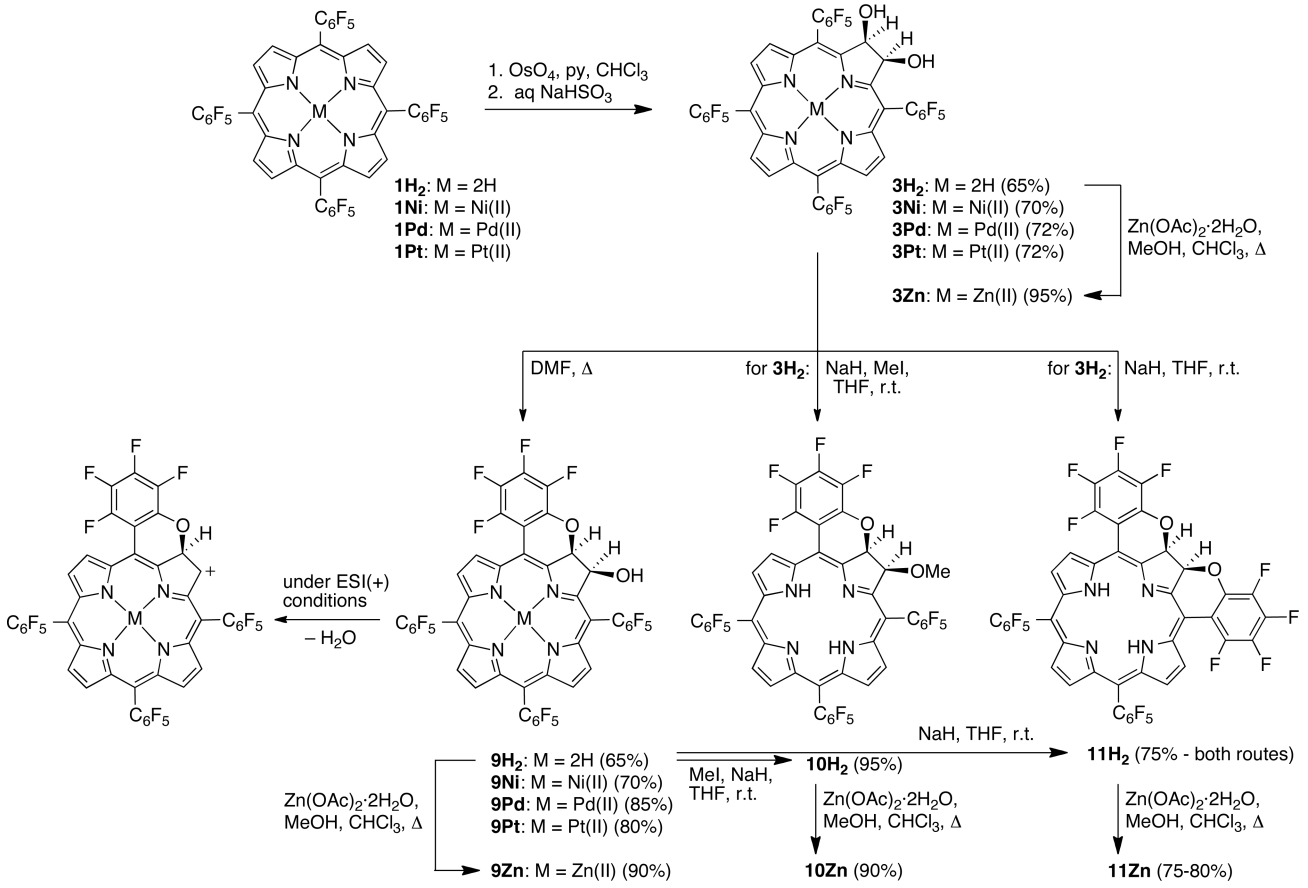
Scheme 2. Synthesis of Mono- and Bis-chromene-Annulated Chlorins 9−11 and Their Metal Complexes



porphyrins and corroles undergo a loss of successive equivalents of HF, forming molecules that contain *β*-to-*o*-phenyl linkages.[37] However, the ^{1}H NMR spectra of the products showed the presence of six *β*-protons—the same number as in the starting material. Other indications also supported the notion that the *β*-positions were not involved in the reaction but that one hydroxyl group of the pyrrolidine diol functionality was involved in the formation of a link to the *o*-phenyl groups instead. Furthermore, the second alcohol functionality of the diol remained intact. For example, the predominant fragment ion in the ESI(+) MS of **9** was the cation resulting from the loss of H_2O from the parent protonated ion (MH^+) (Scheme 2). The formation of these particularly stabilized cations are diagnostic for the presence of hydroxy groups on the pyrrolidine carbons.[21,38] Also, reaction of chlorin diol free base $\mathbf{3H_2}$ with NaH and MeI formed $\mathbf{10H_2}$, the monomethylated analogue to $\mathbf{9H_2}$. The ether $\mathbf{10H_2}$ can also be made directly from alcohol $\mathbf{9H_2}$ by a Williamson ether synthesis. Both the alcohols $\mathbf{9H_2/9M}$ and the corresponding methoxy derivatives $\mathbf{10H_2/10M}$ possess identical optical properties.

As we will delineate in more detail below, all spectroscopic data point toward chlorins $\mathbf{9H_2/9M}$ to possess the novel annulated chlorin structures shown. Thus, an intramolecular S_NAr reaction between one hydroxy group of the diol moiety in *meso*-tetrakis(pentafluorophenyl)-2,3-dihydroxychlorin $\mathbf{3H_2/3M}$ and the *o*-position of the flanking pentafluorophenyl group generated the *β*-to-*o*-aryl oxygen link. This results in the annulation of a (reduced) 2-benzopyrane moiety to the chlorin framework. Since reduced 2-benzopyranes are also known as chromenes,[39] we suggest to refer to chlorins of type **9** and **10** as chromene-annulated chlorins.

We know of no precedent within the chemistry of porphyrinoids for this linkage or the reaction that lead to its formation. Most closely related is an S_NAr reaction of the *p*-F on the pentafluorophenyl groups of $\mathbf{1H_2}$ that was followed by an intramolecular S_NAr reaction that replaced a *m*-F (Scheme 3).[15] This reaction suggests that *p*ara-substituted porphyrins, such as **2**, are likely still susceptible to an intramolecular S_NAr to form, for instance, the corresponding chromene-annulated chlorin. However, it is less clear if the now much more electron-rich tetrafluorophenol groups in **9**/**10** are susceptible to an intermolecular S_NAr reaction at their *p*-positions. We are currently investigating both reaction pathways toward the formation of functionalized chlorins.

Modeling of Chromene-Annulated Chlorin $\mathbf{10H_2}$. In the absence of a crystal structure of any of the chromene-annulated chlorins, we estimated the conformation and bond distances in $\mathbf{10H_2}$ by computer modeling (Figure 1).[40] Irrespective of the chromene annulation, the chlorin macrocycle deviates only little from the slightly nonplanar conformation observed in, for instance, 2,3-dimethoxychlorin.[21] The $C_\alpha-C_{meso}-C_{ipso}-C_o$ dihedral angles associated with the linked aryl group are significantly less than half of the 80−90° angles found in the other three aryl groups. Higher level calculations of chlorins have previously demonstrated the broad conformational trough of chlorins.[41] Thus, we deem the PM3-level model to be a realistic representation of $\mathbf{10H_2}$. In fact, spectroscopic evidence presented below directly support some details of the computed structure.

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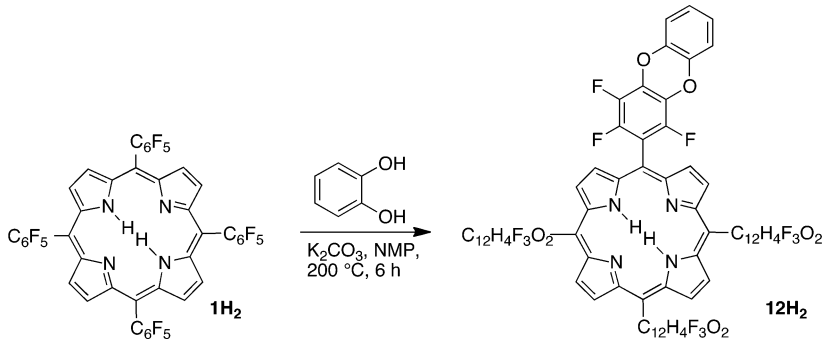
Scheme 3. Synthesis of Catechol-Substituted Porphyrin $12H_2$.[15]



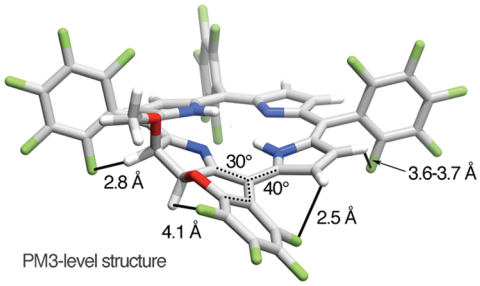


Figure 1. PM3 model of $10H_2$.[38]

^{1}H NMR Spectroscopic Characterization of the Chromene-Annulated Chlorins. A comparison of the ^{1}H NMR spectra of $1H_2$, $3H_2$, $9H_2$, $10H_2$, and $11H_2$ demonstrates the scopes and limits of their diagnostic value (Figure 2). The parent porphyrin $1H_2$ is, on the NMR time scale, 4-fold symmetric and shows only a single s for the β-protons. Dihydroxylation reduces the symmetry elements inherent to dihydroxychlorin $3H_2$ to a mirror plane (the compound is a *meso*-compound) as indicated by the d, s, and overlaying d pattern for the signals assigned to the β-protons and the single s, 2H, for the pyrrolidine H (plus a br s at −2.03 ppm for the inner NH protons, not shown). Upon formation of $9H_2$, the mirror plane is lost and a compound of no apparent planar or axial symmetry is formed (in fact, the compound is chiral): five partially overlaying d and one dd for the β-protons and a splitting of the pyrrolidine H become visible (in addition to the signals for the inner NHs, not shown). The alkylation of $9H_2$, forming $10H_2$, does not change the β- or NH-proton region fundamentally but it simplifies the pyrrolidine-H signals as it removes the ^3J-coupling between the OH group and the *gem*-H. Thus, only the *vic*-coupling between the two nonequivalent pyrrolidine-Hs remains. H,H COSY NMR spectra allow the pairing of the β-Hs in $9H_2$ and $10H_2$ into three groups, corresponding to the three pyrrole building blocks. The spectra of the metal complexes of $3H_2$/$9H_2$ are very similar to those of the free bases shown. The analytical data combined with the ^{1}H NMR data support the connectivity of compounds $9H_2$ and $10H_2$ as the chromene-annulated structures shown.[42] However, direct evidence of the β-to-*o*-fusion, as seen in the ^{1}H NMR spectra of other *meso*-phenyl-substituted porphyrinoids containing such linkages,[23,25,36,43] cannot be derived.

The dd coupling pattern for the most low-field shifted β-proton seen in **9**/**10** remained initially unexplained. A ^4J-coupling to the inner NH could be excluded as addition of D_2O did not remove this coupling in the free bases $9H_2$/$10H_2$, and the Zn(II), Ni(II), Pd(II), and Pt(II) complexes **9M**/**10M** showed an identical coupling. A scalar coupling to the next ^{19}F atom six bonds away also appeared not to be realistic. However, the chromene-annulated structure of **9**/**10** (and, as will be shown below, doubly fused system $11H_2$) implies that the linked fluorophenyl group is brought toward greater coplanarity with the chlorin mean plane. This brings the *o*-fluorine atom and the adjacent β-hydrogen into close proximity to each other, a circumstance well illustrated by the molecular model of $10H_2$ (Figure 1). Indeed, a ^{1}H−^{19}F HOESY spectrum shows a coupling between the β-hydrogen (H^a at 9.00 ppm) and the fluorine atom F^a (at −141.5 ppm), assigned to be the neighboring *o*-fluorine (Figure 3) (for a further assignment of the ^{19}F NMR signals, see below). Indirect nuclear spin−spin couplings of nuclei lacking a formal covalent bond between them but brought into close contact to each other (i.e., pushed together to a distance that results in a nonzero overlap integral), including the "through-space" fluorine−hydrogen coupling tensor, can be understood in terms of a Fermi-contact mechanism.[44] In fact, the molecular model suggests a distance between the *o*-fluorine of the linked aryl group and the adjacent β-hydrogen of 2.5 Å, a value about 0.1 Å shorter than the sum of their van der Waal radii (Figure 1).[45] Such "^6J" H−F couplings were observed before in pentafluorophenylporphyrin derivatives as well as other compounds.[14,30] In comparison, the *o*-F−β-H distances observed in the aryl groups distal to the pyrrolidine moiety are above 3.5 Å.

Other correlations visible in the ^{1}H−^{19}F HOESY NMR spectra of **9M**, for instance, the small interaction between F^a and one pyrrolidine-H, H^g (modeled to be 2.8 Å apart), lend further credence to the assignment of F^a and allow the identification of which other *o*-Fs are adjacent to which β-Hs (the latter of which were grouped into pairs by ^{1}H,^{1}H−COSY NMR spectra, see below). This signal assignment serves as a starting point in the interpretation of the exceedingly well resolved ^{19}F NMR spectra of the compounds of interest (see below), though the small shift differences of H^b, H^c, and H^d do not allow a differentiation of the two pairs of *o*-Fs (F^d) attached to the aryl groups located distal to the pyrrolidine moiety.

Synthesis of Bis-chromene-Annulated Chlorin $11H_2$. Upon reaction of mono-chromene-substituted alcohol $9H_2$ or, more efficiently, dihydroxychlorin $3H_2$ with NaH in the absence of any nucleophile, the formation of a bis-chromene-annulated product $11H_2$ was observed (Scheme 2). Its HR-MS indicated the loss of 2 equiv of HF, and its optical spectra are yet again slightly red-shifted compared to the mono-chromene-substituted system (Figure 6). The symmetry of this *meso*-compound is reflected in its ^{1}H NMR (Figure 2). However, the

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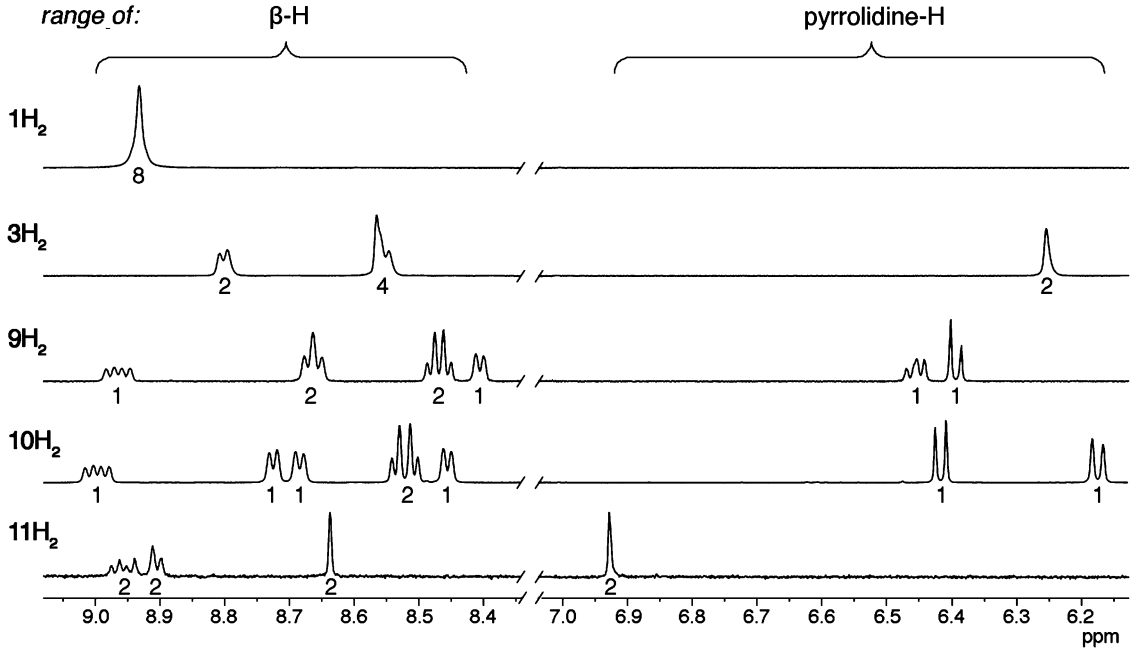

Figure 2. Selected regions of the ^{1}H NMR spectra (400 MHz) of $\mathbf{1H_2}$, $\mathbf{3H_2}$, $\mathbf{9H_2}$, $\mathbf{10H_2}$ (all in $CDCl_3$ at 25 °C), and $\mathbf{11H_2}$ (in DMSO-d_6 at 85 °C, because of limited solubility).

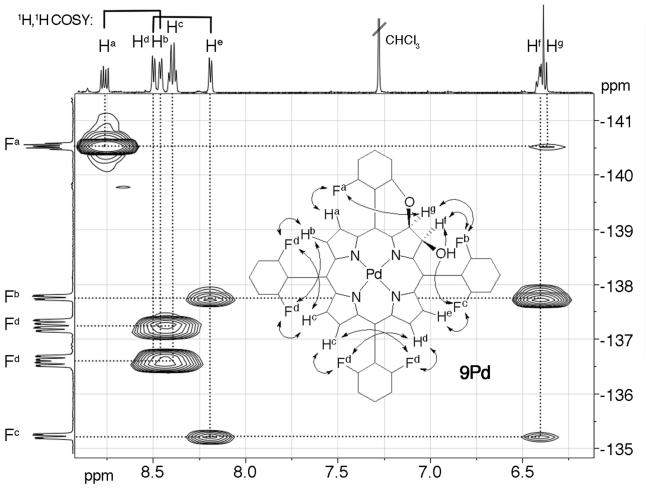

Figure 3. ^{1}H–^{19}F HOESY NMR spectrum (400/376 MHz, $CDCl_3$) of **9Pd**.

solubility of $\mathbf{11H_2}$ is severely reduced compared to the mono-fused systems, limiting the utility of this chlorin.

^{19}F NMR Spectroscopic Characterization of the *meso*-Pentafluorophenylchlorins. The ^{19}F NMR spectra of the chlorins discussed here are most diagnostic. In fact, they are better resolved than the corresponding ^{1}H NMR spectra in most *meso*-aryl-based systems (Figure 4).[20,43,46] Parent (pseudo-)4-fold symmetric porphyrin $\mathbf{1H_2}$ shows the well-known three fluorine resonances for the *o*-, *m*-, and *p*-fluorines.[47] Dihydroxylation of $\mathbf{1H_2}$ reduces the symmetry to 2-fold and, correspondingly, splits all fluorine signals in $\mathbf{3H_2}$ into two groups, whereby both sets of *o*-fluorines are split into two additional sets, reflecting the face differentiation by the *cis*-diol moiety (and imply a slow rotation of the *meso*-aryl groups along the C_{ipso}–C_{meso}). The set distinguished by a 4.5 ppm shift separation is assigned to the *o*-fluorines located on the aryl groups proximal to the pyrrolidine diol moiety. Upon annulation, the 2-fold NMR symmetry is, as expected, lost. For instance, four triplets for the *p*-F are discernible (though two signal overlap) in the spectrum of $\mathbf{9H_2}$. The linkage and concomitant loss of one *o*-F reduces the total integral over all *o*-F atoms to seven. The establishment of a second chromene moiety restores the 2-fold symmetry. Now two classes of *p*-F are visible: those belonging to the linked aryls and those belonging to the distal aryls. Accordingly, the *o*-F split into two groups: one doublet (2F) belonging to the two remaining *o*-F on the linked aryls (that show also the ^{1}H–^{19}F coupling described above) and one doublet (4F) assigned to the distal aryl groups. The two near-co-planar chromene moieties do not affect a face differentiation of these *o*-Fs.

The individual signals in the ^{19}F NMR spectra of the chlorins are, for the most part, well separated from each other and exquisitely detailed, showing the expected and diagnostic coupling patterns (Figure 4). This allows the recording of meaningful ^{19}F–^{19}F COSY spectra that lead to an unambiguous assignment of the majority of the fluorine signals.[48] For instance, the ^{19}F–^{19}F QF-COSY spectrum of **9Pd** allows the correlation, inter alia, of the four F atoms within the chromene moiety (Figure 5).[49] Again, the patterns observed for the free base and metallochlorins are very similar to each other.

Optical Properties of the Chrome-Annulated Chlorins. The UV–vis spectra of the chromene-annulated chlorins and metallochlorins are chlorin and metallochlorin-like, respectively, with a 16 nm red-shift (for λ_{max}) for the mono-chromene-substituted system $\mathbf{9H_2}$ (as well as for the identical spectrum of $\mathbf{10H_2}$), when compared to the starting dihydroxychlorin $\mathbf{3H_2}$ (Figure 6). The bis-annulated chlorin $\mathbf{11H_2}$ red-shifts additional 8 nm. The Soret bands of both annulated chlorins are essentially identical and also red-shifted compared to that of the parent chlorin diol. While the ^{1}H NMR spectra and computed conformation were indicative of the linked *meso*-aryl group to be coplanar enough to be in very close vicinity to the adjacent *β*-H, the aryl group is evidently not coplanar enough to contribute significantly to the chlorin *π*-system. This distinguished these systems from annulated porphyrins such as **6** for

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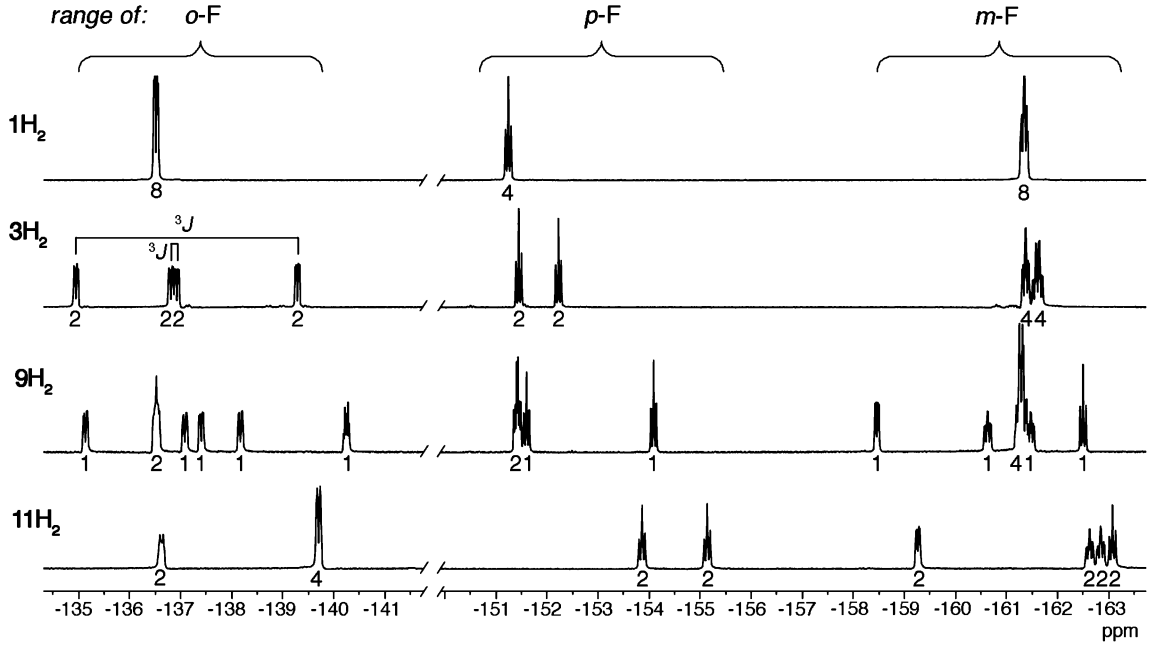

Figure 4. Aryl-F regions of the ^{19}F NMR spectra (376 MHz) of $\mathbf{1H_2}$, $\mathbf{3H_2}$, and $\mathbf{9H_2}$, all in $CDCl_3$ at 25 °C, and $\mathbf{11H_2}$ in DMSO-d_6 at 85 °C (due to limited solubility of this compound in $CDCl_3$ at ambient T).

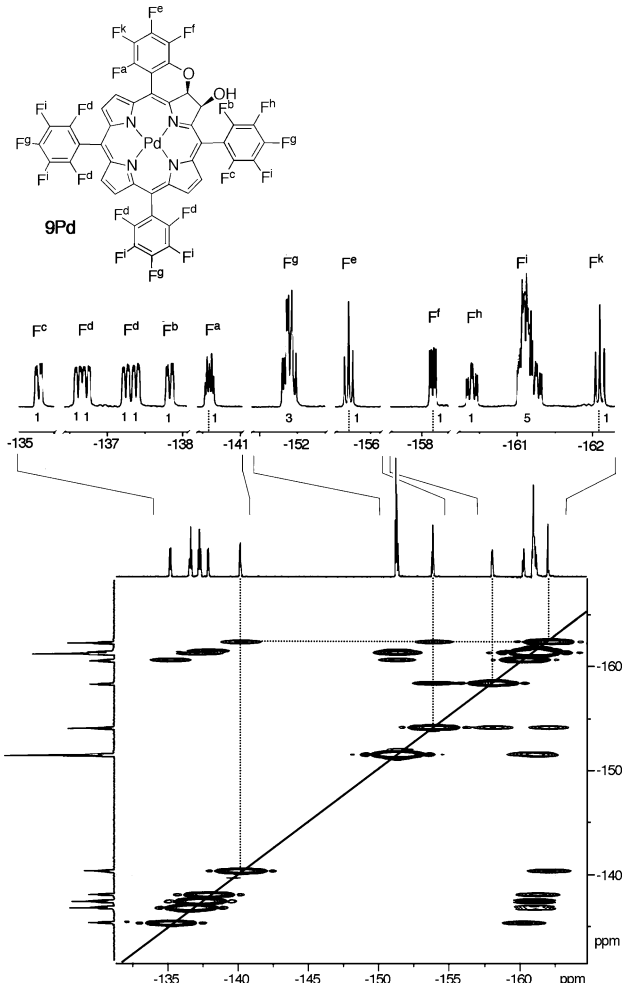

Figure 5. ^{19}F–^{19}F QF-COSY NMR spectrum (376 MHz, $CDCl_3$) of **9Pd**. Correlations indicated only for the fluorine atoms attached to the chromene moiety.

which a 305 nm bathochromic shift of λ_{max} was recorded.[27] On the other hand, annulated porphyrin **5** also exhibits only a shift of 16 nm,[26] even though the five-membered annulated ring suggests a larger degree of coplanarity of the phenyl group and, perhaps, a larger degree of nonplanarity of the chromophore.

Protonation of the chromene-annulated chlorin free bases $\mathbf{9H_2}$ and $\mathbf{11H_2}$ has essentially the same consequences on their optical spectra as it has on the dihydroxychlorin $\mathbf{3H_2}$ (Figure 6). The spectra broaden out, the extinction coefficient erodes by about 20%, and the side bands become less defined without exhibiting a large λ_{max} shift. We interpret the similarity of the chlorin and annulated chlorins as an indication that the conformation and conformational flexibility of the annulated systems is comparable to that of the non-annulated chlorin.

All fluorescence spectra show the typical small Stoke's shift and a chlorin-like intensity distribution of the two band emission spectra. The chromene annulation reduces the fluorescence yield ϕ by about 50% (for $\mathbf{9H_2}$ to 0.17) when compared to chlorin $\mathbf{3H_2}$. This preliminary finding is surprising as the annulation is believed to bring about, if anything, a rigidification of the chromophore with an expected concomitant emission yield increase. However, the conformation of the annulated chlorin is not known for certain, nor can we estimate the change in the conformational flexibility upon annulation, both factors which affect the photophysical parameters of porphyrins.[50] A detailed study of the photophysical and electrochemical properties of the chromene-annulated chlorins is ongoing.

■ CONCLUSIONS

We described an efficient synthesis of free base chromene-annulated chlorins, and their Ni(II), Zn(II), Pd(II), and Pt(II) complexes, by intramolecular nucleophilic aromatic substitution of a *o*-fluorine atom by the alcohol functionality of *meso*-pentafluorophenyl-substituted 2,3-dihydroxychlorins. The annulation red-shifts the λ_{max} of the chromophores only modestly.

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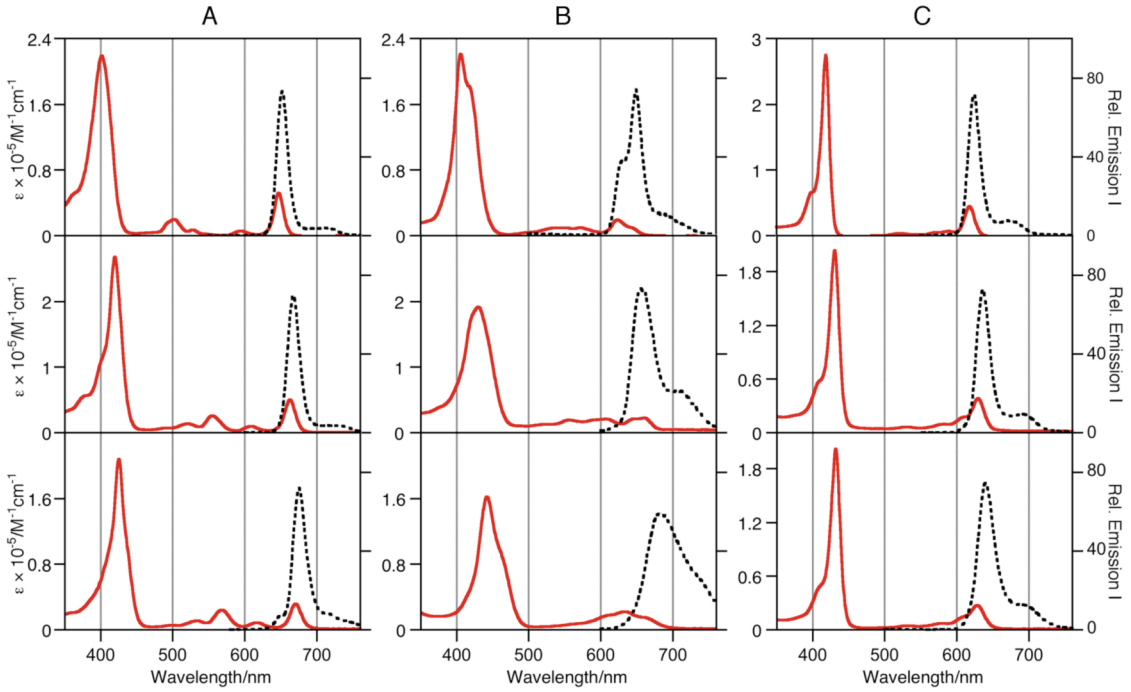

Figure 6. UV−vis (solid traces) and fluorescence emission (dotted traces) spectra of **3H$_2$**, **9H$_2$**, and **11H$_2$** in CH_2Cl_2 (column A), **3H$_2$**, **9H$_2$**, and **11H$_2$** in CH_2Cl_2/5% TFA (column B), and **3Zn**, **9Zn**, and **11Zn** in CH_2Cl_2 (column C); $\lambda_{excitation} = \lambda_{Soret}$ (CH_2Cl_2).

While the nucleophilic substitution of the *p*-fluorine atom in *meso*-tetrakis(pentafluorophenyl)porphyrins was described well in the past, we are not aware of any reports on the (intramolecular) substitution of the *o*-positions. The establishment of the chromene moiety is, based on optical data and molecular modeling, not believed to alter dramatically the conformation and even conformational flexibility of the chlorin moiety. The work presents a model reaction for the modulation of the chromophore of *meso*-pentafluorophenyl-substituted porphyrinoids that takes advantage of the particular reactivity of the pentafluorophenyl groups. This may enhance the chance that these robust chlorins will find utility in technical applications. The scarcity of hydrogens in these systems and $^{19}F-^{13}C$ couplings pose challenges in their characterization by standard ^1H and ^{13}C NMR spectroscopy. This particularly true when, as is the case presented here, the pentafluorophenyl groups are involved in the framework modification of the porphyrin. Therefore, the detailed analysis of the ^{19}F NMR spectra of these chlorins presented may lay the foundation for a more detailed analysis of the ^{19}F NMR spectra of pentafluorophenyl-substituted porphyrinoids of lower symmetry.

EXPERIMENTAL SECTION

Materials and Instrumentation. 5,10,15,20-Tetrakis(pentafluorophenyl)porphyrin **1H$_2$**[4] was purchased from a commercial supplier. The metal complexes **1Ni**, **1Pd**, and **1Pt** were prepared as described in the literature.[4,35,36] Flash column chromatography was performed on an automated flash chromatography system, on normal-phase silica columns (sizes of columns and solvents used are indicated; isochratic eluation modes). The crude products were dry-packed onto silica gel in a precolumn. The fluorescence yields (ϕ) were determined relative to those of *meso*-tetrakisphenylporphyrin (ϕ = 0.11 in benzene,[51] calculated to be 0.09 in CH_2Cl_2); $\lambda_{excitiation} = \lambda_{Soret}$.

5,10,15,20-Tetrakis(pentafluorophenyl)-2,3-*cis*-dihydroxychlorin (3H$_2$) (General Procedure for the Dihydroxylation of Pentafluorophenylporphyrins). 5,10,15,20-Tetrakis(pentafluorophenyl)porphyrin (**1H$_2$**) (1.00 g, 1.03×10^{-3} mol) was dissolved in a 250 mL round-bottom flask equipped with a stir bar in $CHCl_3$ (125 mL) and freshly distilled pyridine (25 mL). The mixture treated with 1 equiv of OsO_4 (1.03×10^{-3} mol; 13.1 mL of a stock solution of 1.0 g OsO_4 dissolved in 50 mL of pyridine). (Caution: use gloves, eye protection, and fume hood!) The flask was stoppered, shielded from light with aluminum foil, and stirred at ambient temperature. The disappearance of the starting material/appearance of the product was monitored by TLC and UV−vis spectroscopy. Once no further progress of the reaction was detectable (after ~24 h), approximately 50% of the solvent was removed by rotary evaporation. To the crude reaction mixture was added a saturated MeOH/H_2O (1:1) solution of $NaHSO_3$ (80 mL). The flask was stoppered and wrapped in aluminum foil, and the biphasic solution was vigorously stirred at ambient temperature for 2 d. Once no further progress of the reaction was detectable by TLC, the mixture was transferred into a 250 mL separatory funnel. The organic fraction was separated with CH_2Cl_2 and filtered through a short plug of diatomaceous earth (Celite). The solvent was removed to dryness by rotary evaporation. A gentle stream of N_2 for several h ensured that the crude material was thoroughly dried. The crude material was purified via flash chromatography (24 g of silica−CH_2Cl_2/1.0%MeOH). After the recovery of the low polarity starting material **1H$_2$** (5−10%), the second major fraction was dihydroxychlorin **3H$_2$** that was isolated in 65−70% yield (570 mg) as a greenish-brown solid: R_f (silica−CH_2Cl_2/1% MeOH) = 0.79; ^1H NMR (400 MHz, $CDCl_3$, δ) 8.77 (d, ^3J = 5.1 Hz, 1H), 8.53−8.52 (m, 2H), 6.22 (d, ^3J = 5.5 Hz, 1H), 3.11 (d, ^3J = 6.3 Hz,1H), −2.03 (s, 1H); ^{19}F NMR (376 MHz, $CDCl_3$, δ) −161.6 (dq, ^3J = 22.7 Hz, ^5J = 8.0 Hz, 2F, F^d), −161.4 (td, ^3J = 21.9 Hz, ^5J = 7.6 Hz, 2F, F^e), −152.2 (t, ^3J = 20.8 Hz, 1F, F^f), −151.4 (t, ^3J = 20.8 Hz, 1F, F^g), −139.3 (dd, ^3J = 24.2 Hz, ^5J = 7.7 Hz, 1F, F^b), −136.9 (dd, ^3J = 24.2, ^5J = 7.7 Hz, 1F, F^c), −136.7 (dd, ^3J = 24.5, ^5J = 8.3 Hz, 1F, F^c), −134.9 (dd, ^3J = 24.1 Hz, ^5J = 7.9 Hz, 1F, F^a);[52] UV−vis (CH_2Cl_2) λ_{max}, nm (log ε) 402 (5.16), 502 (4.14), 528 (3.70), 595 (3.61), 647 (4.54); fluorescence (CH_2Cl_2) λ_{max}, nm 649, ϕ = 0.34; HR-MS (ESI+, 100% CH_3CN) calcd for $C_{44}H_{13}F_{20}N_4O_2$ (MH^+) 1009.0714, found 1009.0696.

[5,10,15,20-Tetrakis(pentafluorophenyl)-2,3-dihydroxychlorinato]Zn(II) (3Zn). In a 250 mL round-bottom flask equipped with a stirring bar and reflux condenser was dissolved 5,10,15,20-tetrakis(pentafluorophenyl)-2,3-dihydroxychlorin (**3H$_2$**) (200 mg, 1.98×10^{-4} mol) in $CHCl_3$ (100 mL) and MeOH (10 mL).

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$Zn(II)(acetate)_2{\cdot}2H_2O$ (174 mg, 7.92×10^{-4} mol, 4 equiv) was added, and the solution was heated to reflux for 3 h. The resulting solution was allowed to cool to room temperature, and the solvent was removed by rotary evaporation. The residue was dissolved in CH_2Cl_2 (10 mL) and purified via flash chromatography (12 g of silica–CH_2Cl_2/1.5% MeOH). Isolated in 92–97% yield (194 mg) as a blue solid: R_f (silica–CH_2Cl_2/1% MeOH) = 0.23; ^{1}H NMR (400 MHz, $CDCl_3$, δ) 8.63 (d, ^3J = 4.4 Hz, 1H), 8.51 (s, 1H), 8.33 (d, ^3J = 4.5 Hz, 1H), 6.17 (s, 1H), 5.75–5.2 (br s, 1H); ^{19}F NMR (376 MHz, $CDCl_3$, δ) −162.9 (br t, ^3J = 22.1 Hz, 2F, F^d), −162.3 (br q, ^3J = 20.8 Hz, ^5J = 7.6 Hz, 2F, F^e), −154.2 (br q, ^3J = 20.6 Hz, ^5J = 7.6 Hz, 1F, F^f), −152.9 (td, ^3J = 20.6 Hz, ^5J = 7.6 Hz, 1F, F^g), −140.1 (br d, ^3J = 24.2 Hz, 1F, F^b), −136.7, −136.6 (overlapping dd, ^3J = 23.8, ^5J = 7.7 Hz, 2F, F^c), −135.4 (dd, ^3J = 24.4 Hz, ^5J = 7.6 Hz, 1F, F^a);[52] UV–vis (CH_2Cl_2) λ_{max}, nm (log ε) 419 (2.75), 618 (0.44); fluorescence (CH_2Cl_2) λ_{max}, nm 624; HR-MS (ESI+, 100% CH_3CN) calcd for $C_{44}H_{11}F_{20}N_4O_2{}^{64}Zn$ (MH^+) 1070.9854, found 1070.9875.

[5,10,15,20-Tetrakis(pentafluorophenyl)-2,3-dihydroxychlorinato]Ni(II) (3Ni). Prepared in 68–74% yield (70 mg) as a green solid from [5,10,15,20-tetrakis(pentafluorophenyl)-porphyrinato]Ni(II) (**1Ni**) (100 mg, 9.71×10^{-5} mol) according to the general procedure for the dihydroxylation of pentafluorophenyl-porphyrins: R_f (silica–CH_2Cl_2/1% MeOH) = 0.72; ^{1}H NMR (400 MHz, $CDCl_3$, δ) 8.38 (d, ^3J = 4.8 Hz, 1H), 8.24 (s, 1H), 8.12 (d, ^3J = 4.7 Hz, 1H), 5.78 (d, ^3J = 6.0 Hz, 1H), 2.95 (d, 7.4 1H); ^{19}F NMR (376 MHz, $CDCl_3$, δ) −161.8 (td, ^3J = 22.4 Hz, ^5J = 7.1 Hz, 1F, F^d), −161.6 (td, ^3J = 22.4 Hz, ^5J = 7.4 Hz, 1F, F^d), −161.1 to −161.2 (m, 2F, F^e), −152.7 (t, ^3J = 20.7 Hz, 1F, F^f), −151.6 (t, ^3J = 20.8 Hz, 1F, F^g), −139.2 (dd, ^3J = 23.8 Hz, ^5J = 7.8 Hz, 1F, F^b), −137.2,-137.3 (overlapping dd, ^3J = 24.6, ^5J = 7.3 Hz, 2F, F^c), −135.6 (dd, ^3J = 23.1 Hz, ^5J = 6.9 Hz, 1F, F^a);[52] UV–vis (CH_2Cl_2) λ_{max}, nm (log ε) 410 (5.10), 501 (4.05), 615 (4.59); HR-MS (ESI+, 100% CH_3CN) calcd for $C_{44}H_{11}F_{20}N_4O_2{}^{58}Ni$ (MH^+) 1064.9911, found 1064.9931.

[5,10,15,20-Tetrakis(pentafluorophenyl)-2,3-dihydroxychlorinato]Pd(II) (3Pd). Prepared in 69–75% yield (172 mg) as a blueish-green solid from [5,10,15,20-tetrakis(pentafluorophenyl)-porphyrinato]Pd(II) (**1Pd**) (240 mg, 2.23×10^{-4} mol) according to the general procedure for the dihydroxylation of pentafluorophenyl-porphyrins: R_f (silica–CH_2Cl_2/2% MeOH) = 0.76; ^{1}H NMR (300 MHz, $CDCl_3$, δ) 8.52 (d, ^3J = 5.0 Hz, 1H), 8.49 (s, 1H), 8.28 (d, ^3J = 5.1 Hz, 1H), 6.20 (br s, 1H), 3.31 (br s, 1H); ^{19}F NMR (376 MHz, $CDCl_3$, δ) −161.8 to −162.1 (m, 2F, F^d), −161.3 (td, ^3J = 21.8 Hz, ^5J = 7.8 Hz, 2F, F^e), −152.8 (t, ^3J = 20.8 Hz, 1F, F^f), −151.5 (t, ^3J = 20.8 Hz, 1F, F^g), −139.3 (dd, ^3J = 23.9 Hz, ^5J = 7.4 Hz, 1F, F^b), −137.0 (br d, ^3J = 21.3 Hz, 2F, F^c), −135.1 (dd, ^3J = 23.8 Hz, ^5J = 7.2 Hz, 1F, F^a);[52] ^{13}C NMR (100 MHz, $CDCl_3$, δ) 166.0, 150.2, 145.7, 145.1, 143.6, 141.1, 139.53, 138.6, 132.3, 128.6, 127.7, 124.8, 109.8, 99.5, 74.4; UV–vis (CH_2Cl_2) λ_{max}, nm (log ε) 402 (5.16), 489 (3.87), 556 (3.97), 597 (4.79); HR-MS (ESI+, 100% CH_3CN) calcd for $C_{44}H_{11}F_{20}N_4O_2{}^{106}Pd$ (MH^+) 1112.9597, found 1112.9617.

[5,10,15,20-Tetrakis(pentafluorophenyl)-2,3-dihydroxychlorinato]Pt(II) (3Pt). Prepared in 68–74% yield (187 mg) as a purple solid from [5,10,15,20-tetrakis(pentafluorophenyl)-porphyrinato]Pt(II) (**1Pt**) (240 mg, 2.23×10^{-4} mol) according to the general procedure for the dihydroxylation of pentafluorophenyl-porphyrins: R_f (silica–CH_2Cl_2/1% MeOH) = 0.60; ^{1}H NMR (300 MHz, $CDCl_3$, δ) 8.56–8.55 (m, 2H), 8.36 (d, ^3J = 5.1 Hz, 1H), 6.23 (br s, 1H), 3.28 (br s, 1H); ^{19}F NMR (376 MHz, $CDCl_3$, δ) −161.5 to 161.8 (m, 2F, F^d), −160.9 to −161.1 (m, 2F, F^e), −152.4 (t, ^3J = 20.9 Hz, 1F, F^f), −151.3 (t, ^3J = 20.9 Hz, 1F, F^g), −139.2 (dd, ^3J = 23.8 Hz, ^5J = 7.3 Hz, 1F, F^b), −136.9 (dd, ^3J = 23.3, ^5J = 7.8 Hz, 2F, F^c), −135.0 (dd, ^3J = 23.8 Hz, ^5J = 7.5 Hz, 1F, F^a);[52] UV–vis (CH_2Cl_2) λ_{max}, nm (log ε) 392 (5.07), 478 (3.66), 551 (3.83), 561 (3.81); HR-MS (ESI+, 100% CH_3CN) calcd for $C_{44}H_{11}F_{20}N_4O_2{}^{195}Pt$ (MH^+) 1202.0214, found 1202.0218.

10,15,20-Tris(pentafluorophenyl)-(5,6,7,8-tetrafluoro-2*H*-chromene-annulated)-2-hydroxychlorin ($9H_2$). 5,10,15,20-Tetrakis(pentafluorophenyl)-2,3-dihydroxychlorin (**3H$_2$**) (500 mg, 4.96×10^{-4} mol) was dissolved in DMF (100 mL) in a 250 mL round-bottom flask equipped with a stirring bar. It was heated to reflux for 40 min. The disappearance of the starting material was monitored by TLC and UV–vis spectroscopy. Once no further progress of the reaction was detectable, the solvent was removed in vacuo and the residue was thoroughly dried under a gentle stream of N_2 for 1 d. The crude material was purified via flash chromatography (24 g of silica gel–CH_2Cl_2/40% hexanes) to provide the product in 60–68% yield (318 mg) as a purple-red solid: R_f (silica–CH_2Cl_2/10% hexanes) = 0.81; ^{1}H NMR (400 MHz, $CDCl_3$, δ) 8.96 (dd, $^3J_{H-H}$ = 5.3, $^6J_{H-F}$ = 9.7 Hz, 1H), 8.68–8.65 (t, ^3J = 5.4 Hz, 2H), 8.49–8.45 (q, ^3J = 5.0 Hz, 2H), 8.40 (d, ^3J = 4.6 Hz, 1H), 6.47–6.44 (m, 1H), 6.39 (d, ^3J = 6.5 Hz, 1H), 2.90 (d, ^3J = 4.6 Hz, 1H), −0.69 (s, 1H), −1.01 (s, 1H); ^{19}F NMR (376 MHz, $CDCl_3$, δ) −162.5 (t, ^3J = 21.7 Hz, 1F, F^k), −161.2 to −161.6 (m, 5F, F^i), −160.6 (td, ^3J = 22.4, ^5J = 7.6 Hz, 1F, F^h), −158.5 (dd, ^3J = 21.0, ^5J = 9.2 Hz, 1F, F^f), −154.1 (t, ^3J = 21.0 Hz, 1F, F^e), −151.6 (t, ^3J = 20.9 Hz, 1F, F^g), −151.4 (td, ^3J = 20.8, ^5J = 9.9 Hz, 2F, F^g), −140.2 to −140.3 (m,1F, F^a), −138.2 (dd, ^3J = 24.2, ^5J = 7.5 Hz, 1F, F^b), −137.4 (dd, ^3J = 23.3, ^5J = 6.5 Hz, 1F, F^d), −137.1 (dd, ^3J = 24.1, ^5J = 6.8 Hz, 1F, F^d), −136.5 to −136.6 (m, 2F, F^d), −135.1 (dd, ^3J = 23.9, ^5J = 7.9 Hz, 1F, F^c);[52] UV–vis (CH_2Cl_2) λ_{max}, nm (log ε) 419 (5.43), 520 (4.13), 556 (4.41), 610 (3.98), 663 (4.70); fluorescence (CH_2Cl_2) λ_{max}-emission, nm 668, ϕ = 0.17; HR-MS (ESI+, 100% CH_3CN) calcd for $C_{44}H_{12}F_{19}N_4O_2$ (MH^+) 989.0657, found 989.0629.

10,15,20-Tris(pentafluorophenyl)-(5,6,7,8-tetrafluoro-2*H*-chromene-annulated)-2-hydroxychlorinato]Zn(II) (9Zn). Prepared in 90–95% yield (67 mg) as a green solid from free base **9H$_2$** (70 mg, 7.10×10^{-5} mol) in $CHCl_3$ (80 mL), MeOH (10 mL), and $Zn(II)(acetate)_2{\cdot}2H_2O$ (3.55×10^{-4} mol, 78 mg, 5 equiv), reflux 4 h, according to procedure for the preparation of **3Zn**. Purification via flash chromatography (4 g of silica–CH_2Cl_2/1.5%MeOH): R_f (silica-CH_2Cl_2) = 0.15; ^{1}H NMR (400 MHz, $CDCl_3$, δ) 8.79 (dd, $^3J_{H-H}$ = 4.7 Hz, J_{H-F} = 10.9 Hz, 1H), 8.50 (d, ^3J = 4.7 Hz, 1H), 8.33 (d, ^3J = 4.6 Hz, 1H), 8.29 (br s, 2H), 7.92 (d, ^3J = 4.6 Hz, 1H), 6.11 (d, ^3J = 6.3 Hz, 1H), 6.00 (d, ^3J = 6.3 Hz, 1H); ^{19}F NMR (376 MHz, $CDCl_3$, δ) −162.8 (t, ^3J = 21.8 Hz, 1F, 1F^k), −162.1 (td, ^3J = 22.3, ^5J = 7.5 Hz, 1F, F^i), −161.7 to −161.9 (m, 3F, F^i), −161.6 (td, ^3J = 22.3, ^5J = 7.4 Hz, 1F, F^i), −161.1 (td, ^3J = 22.3, ^5J = 7.5 Hz, 1F, F^h), −159.2 (dd, ^3J = 21.0, ^5J = 8.5 Hz, 1F^f), −156.0 (t, ^3J = 21.0 Hz, 1F, F^e), −152.6 (t, ^3J = 20.7 Hz, 1F, F^g), −152.3, −152.4 (overlapping t, ^3J = 20.7 Hz, 2F, F^g), −140.4 to −140.5(m, 1F, F^a), −138.5 to −138.6 (m, 2F, F^d), −137.9 (dd, ^3J = 23.8, ^5J = 7.0 Hz, 1F, F^b), −137.0, −137.2 (overlapping dd, ^3J = 23.4, ^5J = 6.6 Hz, 3F, F^{c,d});[52] UV–vis (CH_2Cl_2) λ_{max}, nm (log ε) 428 (5.27), 630 (4.58); fluorescence (CH_2Cl_2) λ_{max}, nm 636, 690; HR-MS (ESI+, 100% CH_3CN) calcd for $C_{44}H_{10}F_{19}N_4O_2{}^{64}Zn$ (MH^+) 1050.9792, found 1050.9765.

[10,15,20-Tris(pentafluorophenyl)(5,6,7,8-tetrafluoro-2*H*-chromene-annulated)-2-hydroxychlorinato]Ni(II) (9Ni). Prepared in 71–76% yield (34 mg) as a green solid from [5,10,15,20-tetrakis(pentafluorophenyl)-2,3-dihydroxychlorinato]Ni(II) (**3Ni**) (50 mg, 4.69×10^{-5} mol) according to the procedure described for the synthesis of free base **9H$_2$**: R_f (silica–CH_2Cl_2/50% hexanes) = 0.25; ^{1}H NMR (400 MHz, $CDCl_3$, δ) 8.52 (dd, $^3J_{H-H}$ = 5.1 Hz, $^6J_{H-F}$ = 8.4 Hz, 1H), 8.38 (d, ^3J = 5.0 Hz, 1H), 8.31 (d, ^3J = 4.9 Hz, 1H), 8.18 (d, ^3J = 4.8 Hz, 1H), 8.14 (d, ^3J = 4.9 Hz, 1H), 7.98 (d, ^3J = 4.8 Hz, 1H), 6.09 (d, ^3J = 6.1 Hz, 1H), 6.05 (br d, ^3J = 6.0 Hz, 1H), 2.99 (s, 1H); ^{19}F NMR (376 MHz, $CDCl_3$, δ) −162.3 (t, ^3J = 21.7 Hz, 1F, F^k), −160.9 to 161.4 (m, 5F, F^i), −160.1 (td, ^3J = 22.3, ^5J = 7.9 Hz, 1F, F^h), −158.2 (dd, ^3J = 20.8, ^5J = 9.4 Hz, 1F, F^f), −154.7 (t, ^3J = 20.9 Hz, 1F, F^e), −151.4, −151.5 (overlapping t, ^3J = 20.9 Hz, 2F, F^g), −151.3 (t, ^3J = 20.9 Hz, 1F, F^g), −142.5 to −142.6 (m, 1F, F^a), −137.6 (dt, ^3J = 25.9, ^5J = 5.5 Hz, 2F, F^d), −137.4 (dd, ^3J = 23.5, ^5J = 5.5 Hz, 1F, F^b), −136.9 (dd, ^3J = 23.3, ^5J = 6.2 Hz, 1F, F^d), −136.7 (dd, ^3J = 23.7, ^5J = 6.5 Hz, 1F, F^d), −136.1 (dd, ^3J = 23.7, ^5J = 7.4 Hz, 1F, F^c);[52] UV–vis (CH_2Cl_2) λ_{max}, nm (log ε) 423 (4.95), 483 (3.46), 627 (4.33); HR-MS (ESI+, 100% CH_3CN) calcd for $C_{44}H_{10}F_{19}N_4O_2{}^{58}Ni$ (MH^+) 1044.9854, found 1044.9867.

[10,15,20-Tris(pentafluorophenyl)-(5,6,7,8-tetrafluoro-2*H*-chromene-annulated)-2-hydroxy-chlorinato]Pd(II) (9Pd). Prepared in 83–90% yield (229 mg) as a dark green solid from [5,10,15,20-tetrakis(pentafluorophenyl)-2,3-dihydroxychlorinato]Pd-(II) (**3Pd**) (270 mg, 2.53×10^{-4} mol) according to the procedure

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described for the synthesis of free base **9H$_2$**: R_f (silica–CH_2Cl_2/50% hexanes) = 0.25; ^{1}H NMR (400 MHz, $CDCl_3$, $^3J_{H-H}$ = 5.1 Hz, J_{H-F} =10.3 Hz, 1H), 8.50 (d, ^3J = 5.1 Hz, 1H), 8.46 (d, ^3J = 4.8 Hz, 1H), 8.42–8.38 (m, 2H), 8.19 (d, ^3J = 4.8 Hz, 1H), 6.43–6.39 (m, 1H), 6.42 (d, 6.8 Hz, 1H), 3.06–3.05 (br s, 1H); ^{19}F NMR (376 MHz, $CDCl_3$, δ) −162.1 (t, ^3J = 21.8 Hz, 1F, F^k), −161.0 to 161.3 (m, 5F, F^i), −160.4 (td, ^3J = 22.3, ^5J = 7.7 Hz, 1F, F^h), −158.1 (dd, ^3J = 21.0, ^5J = 9.3 Hz, 1F, F^f), −154.2 (t, ^3J = 20.9 Hz, 1F, F^e), −151.3 to −151.5 (m, 3F, F^g), −140.5 to −140.6 (m, 1F, F^a), −137.8 (dd, ^3J = 23.9, ^5J = 7.8 Hz, 1F, F^b), −137.4 (dd, ^3J = 23.7, ^5J = 5.5 Hz, 1F, F^d), −137.2 (dd, ^3J = 23.8, ^5J = 5.8 Hz, 1F, F^d), −136.7 (dd, ^3J = 23.8, ^5J = 6.5 Hz, 1F, F^d), −136.6 (dd, ^3J = 23.8, ^5J = 7.0 Hz, 1F, F^d), −135.3 (dd, ^3J = 23.8, ^5J = 8.0 Hz, 1F, F^c);[52] UV–vis (CH_2Cl_2) λ_{max}, nm (log ε) 419 (4.99), 502 (3.57), 546 (3.66), 571 (3.85), 610 (4.49); HR-MS (ESI+, 100% CH_3CN) calcd for $C_{44}H_{10}F_{19}N_4O_2{}^{106}Pd$ (MH^+) 1092.9537, found 1092.9509.

[10,15,20-Tris(pentafluorophenyl)-(5,6,7,8-tetrafluoro-2*H*-chromene-annulated)-2-hydroxychlorinato]Pt(II) (9Pt). Prepared in 80–85% yield (37 mg) as a blue-green solid, from [5,10,15,20-tetrakis(pentafluorophenyl)-2,3-dihydroxychlorinato]Pt-(II) (**3Pt**) (48 mg, 3.99 × 10^{-5} mol) according to the procedure described for synthesis of free base **9H$_2$**: R_f (silica–CH_2Cl_2/50% hexanes) = 0.25; ^{1}H NMR (400 MHz, $CDCl_3$, δ) 8.81 (dd, $^3J_{H-H}$ = 5.1 Hz, J_{H-F} =10.4 Hz, 1H), 8.52–8.44 (m, 4H), 8.28 (d, ^3J = 4.9 Hz, 1H), 6.44 (d, ^3J = 6.4 Hz, 1H), 6.36 (d, ^3J = 6.5 Hz, 1H), 3.09 (s, 1H); ^{19}F NMR (376 MHz, $CDCl_3$, δ) −162.0 (t, ^3J = 21.8 Hz, 1F, F^k), −160.9 to 161.2 (m, 5F, F^i), −160.3 (td, ^3J = 22.3, ^5J = 7.9 Hz, 1F, F^h), −158.1 (dd, ^3J = 20.9, ^5J = 9.2 Hz, 1F, F^f), −153.9 (t, ^3J = 21.0 Hz, 1F, F^e), −151.2 to −151.4 (m, 3F, F^g), −140.0 to −140.2 (m, 1F, F^a), −137.9 (dd, ^3J = 23.6, ^5J = 7.0 Hz, 1F, F^b), −137.2 (dt, ^3J = 23.5, ^5J = 7.2 Hz, 2F, F^d), −136.6 (dt, ^3J = 23.5, ^5J = 7.2 Hz, 2F, F^d), −135.2 (dd, ^3J = 23.5, ^5J = 7.2 Hz, 1F, F^c);[52] UV–vis (CH_2Cl_2) λ_{max}, nm (log ε) 409 (5.60), 489 (4.38), 565 (4.56), 600 (5.13); HR-MS (ESI+, 100% CH_3CN) calcd for $C_{44}H_{10}F_{19}N_4O_2Pt$ (MH^+) 1182.0152, found 1182.0119.

10,15,20-Tris(pentafluorophenyl)-(5,6,7,8-tetrafluoro-2*H*-chromene-annulated)-2-methoxychlorin (10H$_2$). *meso*-Tetrakis-(pentafluorophenyl)-2,3-*cis*-dihydroxychlorin (**3H$_2$**) (100 mg, 9.92 × 10^{-5} mol) was, under N_2, dissolved in 100 mL of THF in a 250 mL round-bottom flask equipped with a magnetic stir bar. First, CH_3I (0.10 mL, 16-fold molar excess) was added by syringe. (Caution: use gloves and fume hood!) Second, excess NaH (~40 mg of a 60% emulsion in mineral oil) was added in portions. The reaction mixture was allowed to stir for ~1 h at ambient temperature. The completion of the reaction was monitored by TLC. After all of the starting material was consumed, the reaction was quenched by slow addition of a concd aq NH_4Cl solution, the mixture was transferred into a separatory funnel, and the product was extracted with CH_2Cl_2. The organic phase was evaporated to dryness by rotary evaporation, and the residue was purified via flash chromatography (4 g of silica–CH_2Cl_2/20% hexanes). Isolated in 90–96% yield (89 mg) as a purple-red solid: R_f (silica–CH_2Cl_2/50% hexanes) = 0.61; ^{1}H NMR (400 MHz, $CDCl_3$, δ) 8.99 (dd, $^3J_{H-H}$ = 5.0 Hz, J_{H-F} = 9.9 Hz, 1H), 8.72 (d, ^3J = 4.8 Hz, 1H), 8.68 (d, ^3J = 5.0 Hz, 1H), 8.53 (d, ^3J = 4.7 Hz, 1H), 8.51 (d, 4.7 Hz, 1H), 8.45 (d, ^3J = 4.9 Hz, 1H), 6.41 (d, ^3J = 6.7 Hz, 1H), 6.17 (d, ^3J = 6.7 Hz, 1H), 3.34 (s, 3H). −0.70 (s, 1H), −1.03 (s, 1H); ^{19}F NMR (376 MHz, $CDCl_3$, δ) −163.0 (t, ^3J = 21.7 Hz, 1F, F^k), −161.0 to −161.5 (m, 6F, F^{h,i}), −158.7 (dd, ^3J = 20.9, ^5J = 9.3 Hz, 1F, F^f), −154.3 (t, ^3J = 21.0 Hz, 1F, F^e), −151.3 to −151.6 (m, 3F, F^g), −140.4 to −140.5 (m, 1F, F^a), −137.9 (dd, ^3J = 24.0, ^5J = 7.7 Hz, 1F, F^b), −137.4 (dd, ^3J = 23.9, ^5J = 6.7 Hz, 1F), −137.1 (dd, ^3J = 23.7, ^5J = 6.7 Hz, 1F, F^d), −136.5 to −136.6 (m, 2F, F^d), −135.4 (dd, ^3J = 23.7, ^5J = 7.9 Hz, 1F, F^c);[52] ^{13}C NMR (100 MHz, $CDCl_3$, δ) 158.2, 158.1, 153.6, 153.1, 145.4, 145.2, 145.2, 143.6, 140.3, 138.2, 135.1, 133.4, 132.9, 128.0, 127.8, 125.9, 123.7, 115.4, 115.4, 115.4, 115.3, 115.2, 115.2, 115.1, 115.1, 115.0, 114.98, 114.94, 114.3, 114.2, 113.6, 113.5, 113.4, 113.4, 107.7, 106.9, 99.0, 97.2, 83.7, 81.5, 59.2; UV–vis (CH_2Cl_2) λ_{max}, nm (log ε) 420 (5.39), 520 (4.06), 555 (4.34), 609 (3.88), 663 (4.63); fluorescence (CH_2Cl_2) λ_{max}, nm 674, ϕ = 0.16; HR-MS (ESI+, 100% CH_3CN) calcd for $C_{45}H_{14}F_{19}N_4O_2$ (MH^+) 1003.0813, found 1003.0844.

[10,15,20-Tris(pentafluorophenyl)-(5,6,7,8-tetrafluoro-2*H*-chromene-annulated)-2-methoxy-chlorinato]Zn(II) (10Zn). Free base chromene-fused chlorin **10H$_2$** (50 mg, 4.99 × 10^{-5} mol) was dissolved in a 250 mL round-bottom flask equipped with a stir bar and reflux condenser in $CHCl_3$ (80 mL) and MeOH (10 mL). Excess Zn(II)(acetate)$_2$·$2H_2O$ (55 mg, 2.49 × 10^{-4} mol, 5 equiv) was added, and the solution was heated to reflux for 4 h. The resulting solution was allowed to cool to room temperature and the solvent was removed by rotary evaporation. The residue was dissolved in CH_2Cl_2 (10 mL) and purified via flash chromatography (4 g of silica–CH_2Cl_2/20% hexanes). Isolated in 90–95% yield (47 mg) as a green solid: R_f (silica–CH_2Cl_2) = 0.78; ^{1}H NMR (400 MHz, $CDCl_3$, δ) 8.71 (dd, $^3J_{H-H}$ = 4.7 Hz, J_{H-F} = 10.5 Hz, 1H), 8.49–8.46 (m, 2H), 8.36 (d, ^3J = 4.4 Hz, 1H), 8.33 (d, 4.5 Hz, 1H), 8.11 (d, ^3J = 4.5 Hz, 1H), 6.29 (d, ^3J = 6.8 Hz, 1H), 5.89 (d, ^3J = 6.8 Hz, 1H), 3.28 (s, 3H); ^{19}F NMR (376 MHz, $CDCl_3$, δ) −163.5 (t, ^3J = 21.8 Hz, 1F, F^k), −161.5 to −163.4 (m, 6F, F^{h,i}), −159.3 (dd, ^3J = 20.8, ^5J = 8.7 Hz, 1F, F^f), −156.0 (t, ^3J = 21.0 Hz, 1F, F^e), −152.2 to −152.5 (m, 3F, F^g), −141.1 to −141.2 (m, 1F, F^a), −138.2 (br d, ^3J = 20.8 Hz, 1F, F^b), −138.0 (br d, ^3J = 20.8 Hz, 1F, F^d), −137.6 (br d, ^3J = 20.8 Hz 1F, F^d), −137.1 to −137.2 (m, 2F, F^d), −135.9 (br d, ^3J = 23.5 Hz, 1F, F^c);[52] UV–vis (CH_2Cl_2) λ_{max}, nm (log ε) 426 (5.11), 627 (4.45); fluorescence (CH_2Cl_2) λ_{max}, nm 644; HR-MS (ESI+, 100% CH_3CN) calcd for $C_{45}H_{12}F_{19}N_4O_2Zn$ (MH^+) 1064.9948, found 1064.9971.

10,15-Bis(pentafluorophenyl)bis(5,6,7,8-tetrafluoro-2*H*-chromene-annulated)chlorin (11H$_2$). Prepared from 5,10,15,20-tetrakis(pentafluorophenyl)-2,3-dihydroxychlorin (**3H$_2$**) (210 mg, 2.08 × 10^{-4} mol) and excess NaH (~100 mg; 60% emulsion in mineral oil) as described for the preparation of **11H$_2$**, except the MeI was omitted. After slow solvent exchange on the rotary evaporator from $CHCl_3$ to EtOH and air drying, the product was obtained as a purple powder in 75–80% yield (155 mg): R_f (silica–CH_2Cl_2/5%MeOH) = 0.78; ^{1}H NMR (400 MHz, at 85 °C, DMSO, δ) 8.95 (dd, $^3J_{H-H}$ = 4.7 Hz, $^6J_{H-F}$ = 9.3 Hz, 1H), 8.90 (d, ^3J = 4.9 Hz, 1H), 8.64 (s, 1H), 6.93 (s, 1H), −0.69 (s, 1H); ^{19}F NMR (376 MHz, $CDCl_3$, δ) −163.1 (t, ^3J = 23.3 Hz, 1F, F^d), −162.8 to −162.9 (m, 1F, F^e) −162.6 to −162.7 (m, 1F, F^e), −152.9.1 (dd, ^3J = 22.4, ^5J = 7.6, Hz, 1F, F^b), −155.1 (t, ^3J = 22.4 Hz, 1F, F^f), −153.9 (t, ^3J = 22.3 Hz, 1F, F^g), −139.7 (br d, ^3J = 22.2, Hz, 2F, F^c), −136.6 to −136.7 (m, 1F, F^a);.[52] UV–vis (CH_2Cl_2) λ_{max}, nm (log ε) 425 (5.31), 534 (4.04), 469 (4.38), 617 (3.93), 671 (4.50); fluorescence (CH_2Cl_2) λ_{max}, nm 676, ϕ = 0.20; HR-MS (ESI+, 100% CH_3CN) calcd for $C_{44}H_{11}F_{18}N_4O_2$ (MH^+) 969.0595, found 969.0611.

[10,15-Bis(pentafluorophenyl)-bis(5,6,7,8-tetrafluoro-2*H*-chromene-annulated)chlorinato]Zn(II) (11Zn). Prepared by zinc insertion into free base bis-chromene-annulated chlorin **11H$_2$** (50 mg, 5.16 × 10^{-5} mol) in $CHCl_3$ (60 mL) and MeOH (10 mL) and excess Zn(acetate)$_2$·$2H_2O$ (57 mg, 2.58 × 10^{-4} mol, 5 equiv) as described for preparation of **10Zn**. Purification via flash chromatography (4 g of silica–CH_2Cl_2/1.5% MeOH). Isolated in 75–80% yield (39 mg) as a green solid: R_f (silica–CH_2Cl_2/3%MeOH) = 0.9. ^{1}H NMR (400 MHz, DMSO at 85 °C, δ) 8.95 (dd, $^3J_{H-H}$ = 4.7 Hz, J_{H-F} = 9.3 Hz, 1H), 8.90 (d, ^3J = 4.9 Hz, 1H), 8.64 (s, 1H), 6.93 (s, 1H), −0.69 (s, 1H); ^{13}C NMR (100 MHz, DMSO at 85 °C, δ) 157.6, 154.0, 147.5, 147.3, 145.5, 139.0, 136.6, 132.6, 130.1, 127.5, 127.4, 116.0, 109.2, 99.0, 85.9, 79.2, 70.4; UV–vis (CH_2Cl_2) λ_{max}, nm (log ε) 432 (5.31), 627 (4.39); fluorescence (CH_2Cl_2) λ_{max}, nm 640, 686; HR-MS (ESI+, 100% CH_3CN) calcd for $C_{44}H_9F_{18}N_4O_2Zn$ (MH^+) 1030.9730, found 1030.9721.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

^{1}H, ^{13}C, and ^{19}F NMR of all compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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