

Factors Controlling the Spectroscopic Properties and Supramolecular Chemistry of an Electron Deficient 5,5-Dimethylphlorin Architecture

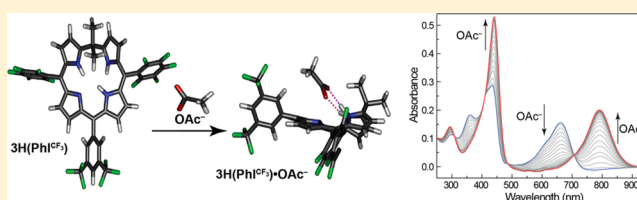
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Supporting Information

ABSTRACT: A new 5,5-dimethylphlorin derivative (**3H**-(**Phl**^{CF₃})) was prepared and studied through a combination of redox, photophysical, and computational experiments. The phlorin macrocycle is significantly distorted from planarity compared to more traditional tetrapyrrole architectures and displays solvatochromism in the Soret region of the UV–vis spectrum (~370–420 nm). DFT calculations indicate that this solvatochromic behavior stems from the polarized nature of the frontier orbital (LUMO+1) that is most heavily involved in these transitions. Compound **3H**-(**Phl**^{CF₃}) also displays an intriguing supramolecular chemistry with certain anions; this phlorin can cooperatively hydrogen-bond two equivalents of fluoride to form **3H**-(**Phl**^{CF₃})·2F[−] but does not bind larger halides such as Cl[−] or Br[−]. Analogous studies revealed that the phlorin can hydrogen-bond with carboxylate anions such as acetate to form 1:1 complexes such as **3H**-(**Phl**^{CF₃})·OAc[−]. These supramolecular assemblies are robust and form even in relatively polar solvents such as MeCN. Hydrogen-bonding of fluoride and acetate anions to the phlorin N–H residues significantly attenuates the redox and photophysical properties of the phlorin. Moreover, The ability to independently vary the size and pK_a of a series of carboxylate hydrogen-bond acceptors has allowed us to probe how phlorin–anion association is controlled by the anion’s size and/or basicity. These studies elucidate the physical properties and the electronic effects that shape the supramolecular chemistry displayed by the phlorin platform.



INTRODUCTION

Porphyrins, corroles, phthalocyanines, and other polypyrrole derivatives display rich photophysical and redox properties that distinguish these platforms for applications that include solar light harvesting,^{1–7} electrogenerated chemiluminescence,^{8–19} and photocatalysis.^{20–25} Additionally, tetrapyrrole macrocycles, such as porphyrinogens and related complexes that contain sp³ hybridized *meso*-carbons,^{26–28} can support an intriguing supramolecular chemistry with anions^{29,30} and multielectron redox properties^{31,32} that can enable energy conversion processes.³³ The lack of π -conjugation between the pyrrole units of such architectures, however, curtails the ability of these systems to absorb visible light.

The 5,5-dimethylphlorin (**3H**(**Phl**)) is a recently developed tetrapyrrole macrocycle in which only one *meso*-carbon is sp³ hybridized. Much like the porphyrinogen, phlorins also support a multielectron redox chemistry and can be reversibly oxidized by up to three electrons. Since π -conjugation is maintained about the entire periphery of the phlorin framework, these systems also display excellent photophysical properties with broad absorbance profiles that span the entire UV–vis spectrum.³⁴ Moreover, because of the nonplanar geometry of the phlorin macrocycle, which is imposed by the single sp³ hybridized *meso*-carbon on the porphyrinoid’s periphery, these

platforms can form robust hydrogen-bonded assemblies with fluoride. Since the phlorin is a strongly absorbing redox active chromophore, the supramolecular association of F[−] with the N–H groups of this macrocycle provides a means to tune both the photophysical and electrochemical properties of these unusual porphyrinoids.³⁴

Although the phlorin’s intriguing physical properties and supramolecular capabilities have started to be uncovered, the underlying factors that drive the unusual electronic structure and compelling anion binding chemistry of this architecture have remained undefined. Previous work has shown that phlorin constructs can strongly bind two equivalents of fluoride via an allosteric/cooperative process, but do not associate with less basic halides (i.e., Cl[−] and Br[−]) to even a minimal extent.³⁴ Hydrogen-bonding of fluoride to the phlorin N–H residues is accompanied by dramatic perturbations to the phlorin absorption profile, making this porphyrinoid an excellent candidate for colorimetric fluoride sensing; however, the factors that drive the phlorin’s exceptional selectivity for fluoride remain unknown. Moreover, the capacity of the phlorin

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macrocycle to form supramolecular assemblies with nonhalide based anions has not previously been documented.

In confronting the limitations in our understanding of the phlorin's properties, we have made use of density functional theory (DFT) calculations in combination with photophysical experiments to help unravel the unusual electronic structure of this little studied porphyrinoid. Moreover, we show for the first time that the 5,5-dimethylphlorin platform can serve as a molecular receptor not only for fluoride but also for sufficiently electron-rich carboxylate anions. In addition to showing that phlorins can access a supramolecular chemistry that is unavailable to more typical porphyrinoids, we have also taken advantage of this carboxylate binding chemistry to help unmask the factors that drive effective anion recognition by the phlorin macrocycle.

■ EXPERIMENTAL SECTION

General Materials and Methods. Reactions were performed in oven-dried round-bottomed flasks unless otherwise noted. Reactions that required an inert atmosphere were conducted under a positive pressure of N₂ using flasks fitted with Suba-Seal rubber septa or in a nitrogen filled glovebox. Air and moisture sensitive reagents were transferred using standard syringe or cannula techniques. Reagents and solvents were purchased from Sigma-Aldrich, Acros, Fisher, Strem, or Cambridge Isotopes Laboratories. Solvents for synthesis were of reagent grade or better and were dried by passage through activated alumina and then stored over 4 Å molecular sieves prior to use.³⁵ Column chromatography was performed with 40–63 μm silica gel with the eluent reported in parentheses. Analytical thin-layer chromatography (TLC) was performed on precoated glass plates and visualized by UV or by staining with KMnO₄. 5,5-Dimethyl-1,9-bis-(pentafluorobenzoyl)dipyrromethane (**1**) was prepared using a previously published method.³⁶ The synthesis of **2** and 3H(Phl^{CF₃}) is detailed in the Supporting Information.

Compound Characterization. ¹H and ¹³C nuclear magnetic resonance (NMR) spectra were recorded at 25 °C on a Bruker 400 MHz spectrometer. Proton spectra are referenced to the residual proton resonance of the deuterated solvent (CDCl₃ = δ 7.26), and carbon spectra are referenced to the carbon resonances of the solvent (CDCl₃ = δ 77.16). All chemical shifts are reported using the standard δ notation in parts-per-million; positive chemical shifts are to higher frequency from the given reference. Low-resolution gas chromatography–mass spectroscopy (LR-GCMS) data were obtained using an Agilent gas chromatograph consisting of a 6850 Series GC System equipped with a 5973 Network Mass Selective Detector. Low resolution MS data was obtained using either a LCQ Advantage from Thermofinnigan or a Shimadzu LC/MS-2020 single quadrupole MS coupled with an high-performance liquid chromatography (HPLC) system, with dual ESI/APCI source. High-resolution mass spectrometry analyses were either performed by the Mass Spectrometry Laboratory in the Department of Chemistry and Biochemistry at the University of Delaware.

UV–Vis Absorption Experiments. UV–visible absorbance spectra were acquired on a StellarNet CCD array UV–vis spectrometer using screw cap quartz cuvettes (7q) of 1 cm path length from Starna. All absorbance spectra were recorded at room temperature. All samples for spectroscopic analysis were prepared in dry solvent within a N₂ filled glovebox. Tetrabutylammonium fluoride (TBAF) titrations were con-

ducted by placing 2.0 mL of 10 μM solutions of 3H(Phl^{CF₃}) into a screw cap quartz cuvette. Following the recording of an initial UV–vis absorbance spectrum, 10 μL aliquots of a 0.25 mM solution of TBAF and phlorin (10 μM) were added to the cuvette and changes in the UV–vis profile were monitored. Since the aliquots were all 10 μM in 3H(Phl^{CF₃}), the concentration of phlorin did not change over the course of the experiment, which significantly simplifies analysis of the titration data. Job analysis for fluoride binding to 3H(Phl^{CF₃}) was carried out using solutions containing 10 μM of total analyte (TBAF + 3H(Phl^{CF₃})). The ratio of 3H(Phl^{CF₃}) to fluoride was systematically varied by combining the appropriately sized aliquots of 10 μM stock solutions of TBAF and phlorin. Titrations and Job analyses conducted for binding of 3H(Phl^{CF₃}) to carboxylate salts were carried out using analogous methods.

Steady-State Fluorescence Measurements. Spectra were recorded on an automated Photon Technology International (PTI) QuantaMaster 40 fluorometer equipped with a 75 W Xenon arc lamp, a LPS-220B lamp power supply, and a Hamamatsu R2658 photomultiplier tube. Samples for fluorescence analysis were prepared in an analogous method to that described above for the preparation of samples for UV–vis spectroscopy. Samples of 3H(Phl^{CF₃}) were excited at λ = 650 nm and emission was monitored from 680–850 nm with a step size of 0.5 nm and integration time of 0.25 s. Reported spectra are the average of at least three individual acquisitions.

Emission quantum yields were calculated using Nile Blue in ethanol (Φ_{ref} = 0.27)³⁷ as the reference actinometer using the expression below,³⁸

$$\Phi_{\text{em}} = \Phi_{\text{ref}} \left(\frac{A_{\text{ref}}}{A_{\text{em}}} \right) \left(\frac{I_{\text{em}}}{I_{\text{ref}}} \right) \left(\frac{\eta_{\text{em}}}{\eta_{\text{ref}}} \right)^2$$

where Φ_{em} and Φ_{ref} are the emission quantum yield of the sample and the reference, respectively, A_{ref} and A_{em} are the measured absorbance of the reference and sample at the excitation wavelength, respectively, I_{ref} and I_{em} are the integrated emission intensities of the reference and sample, respectively, and η_{ref} and η_{em} are the refractive indices of the solvents of the reference and sample, respectively.

Time-Resolved Fluorescence Measurements. The experimental setup for picosecond time-correlated single-photon-counting (TCSPC) measurements has been described in detail previously³⁹ and only a brief account will be given here. The detection system includes an actively quenched single photon avalanche photodiode (PDM 50CT module, Micro Photon Devices) and a TCSPC module (PicoHarp 300, PicoQuant). The light source was an optical parametric amplifier pumped by a 250 kHz Ti:sapphire regenerative amplifier. Excitation was at λ = 650 nm with typically 50 fs (full width at half-maximum, fwhm) pulse duration and <10 nJ pulse energy. Fluorescence emission was selected by using a 10 nm (fwhm) bandpass filter centered at 750 nm (CVI, F10-750.0-4-1.00), which were chosen according to the peak wavelength of the fluorescence emission spectra. The instrument response function (IRF) showed a fwhm of ~40 ps as recorded at the excitation wavelength using a dilute water suspension of coffee creamer. A 4.0 ps channel time was chosen and typically more than 10,000 counts were collected in the peak channel in order to obtain an acceptable signal-to-noise ratio. The polarization of the excitation beam was set to the magic angle (54.7°) with respect to an emission linear polarizer, which enables us to

eliminate any depolarization contribution. Quantitative analysis of the time-resolved fluorescence data were performed by employing a least-squares deconvolution fitting algorithm with explicit consideration of the finite IRF (FluoFit, PicoQuant), and a reduced chi-squared (χ^2) value is used to judge the quality of each fit.

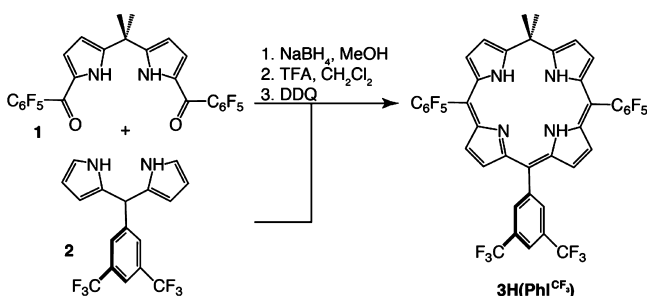
X-ray Crystallography. Crystals of $3\text{H}(\text{Phl}^{\text{CF}_3})$ were mounted using viscous oil onto a plastic mesh and cooled to the data collection temperature. Data were collected on a Bruker-AXS APEX CCD diffractometer with graphite-monochromated Mo- $K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). Unit cell parameters were obtained from 36 data frames, $0.3^\circ \omega$, from three different sections of the Ewald sphere. The systematic absences in the diffraction data are uniquely consistent with the reported space group. The data sets were treated with absorption corrections based on redundant multiscan data. The structures were solved using direct methods and refined with full-matrix, least-squares procedures on F^2 . All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were treated as idealized contributions. Structure factors are contained in the SHELXTL 6.12 program library. The CIF has been deposited under CCDC 960702.

Computations. All density functional calculations were performed using the Gaussian 09 (G09) program package,⁴⁰ with the Becke three-parameter hybrid exchange and Lee–Yang–Parr correlation functional (B3LYP).^{41–43} A 6-31G* basis set was used for all atoms. All geometry optimizations were performed in C_1 symmetry with subsequent vibrational frequency analysis to confirm that each stationary point was a minimum on the potential energy surface. A polarizable continuum model was utilized in the geometry optimization to model the solvent effects of the system.^{44–48} The vertical singlet transition energies of the complexes were computed at the time-dependent density functional theory (TDDFT) level in methylene chloride within G09 by using the optimized ground state structure.

RESULTS AND DISCUSSION

A new 5,5-dimethylphlorin construct containing pentafluorophenyl substituents at the 10- and 20-positions and a bis-trifluoromethylphenyl substituent at the 15-position was prepared using the modular synthetic methodology shown in Scheme 1.^{34,49} Reduction of the diacylated dipyrromethane (**1**) with NaBH_4 in THF/MeOH (3:1) generated the corresponding dicarbinol, which was condensed with 5-(3,5-bis-trifluoromethylphenyl)-dipyrromethane (**2**) in the presence of trifluoroacetic acid (TFA). Subsequent oxidation with DDQ delivered the desired phlorin ($3\text{H}(\text{Phl}^{\text{CF}_3})$) in 41% yield. The

Scheme 1. Synthesis of $3\text{H}(\text{Phl}^{\text{CF}_3})$



solid-state structure of this compound is shown in Figure 1, with corresponding crystallographic parameters and structural metrics provided in the Supporting Information. Compound $3\text{H}(\text{Phl}^{\text{CF}_3})$ represents only the second 5,5-dimethylphlorin derivative for which an X-ray diffraction structure has been determined. Unlike typical porphyrinoids, the $3\text{H}(\text{Phl}^{\text{CF}_3})$ macrocycle is significantly puckered, as the N–H protons on the side of the phlorin containing the 5,5-dimethyl substituents is displaced by $\sim 1.3 \text{ \AA}$ above the plane approximated by the opposite dipyrrole unit of the macrocycle. This structure is reminiscent of that observed for a homologous phlorin containing pentafluorophenyl groups at all three sp^2 hybridized *meso*-carbons.³⁴

Solutions of $3\text{H}(\text{Phl}^{\text{CF}_3})$ in CH_2Cl_2 are emerald in color and are characterized by the blue UV–vis absorption profile shown in Figure 2a. In order to gain insight about the nature of the electronic transitions observed for this porphyrinoid, density functional theory (DFT) and time-dependent DFT (TDDFT) calculations were undertaken for $3\text{H}(\text{Phl}^{\text{CF}_3})$. These calculations revealed that the dominant transitions involve frontier molecular orbitals with significant electron density across all four pyrroles of the phlorin (Figures 2c and S1, Supporting Information). These molecular orbitals are reminiscent of those described by Gouterman in his standard four orbital model of porphyrin electronic structure, with some distortion due to reduction of symmetry from D_{4h} .^{50–53} Calculations showed a notable exception in this regard, as the orbital density of the LUMO+1 of $3\text{H}(\text{Phl}^{\text{CF}_3})$ is not equally distributed about the entire tetrapyrrole framework. Instead, the LUMO+1 is polarized with increased electron density on the side of the phlorin opposite the sp^3 hybridized *meso*-carbon.

Since the LUMO+1 shows distinct asymmetry with respect to electron density about the phlorin periphery, we rationalized that the electronic transitions of $3\text{H}(\text{Phl}^{\text{CF}_3})$ between states that involve the LUMO+1 should display charge transfer character and therefore be sensitive to the polarity of the surrounding environment. Comparison of the UV–vis absorbance profiles obtained for $3\text{H}(\text{Phl}^{\text{CF}_3})$ in a variety of solvents clearly shows that the phlorin displays solvatochromism (Figure 2a). Since the major transitions at $\sim 440 \text{ nm}$ involve excited state population of the LUMO+1, changes in the solvent polarity would be expected to perturb the energy of these bands. As shown in Figure 2b, as the polarity of the solvent is increased, the *soret* absorbance shifts from 442 nm in benzene, which has a dielectric constant of $\epsilon = 2.3$ to 435 nm in acetonitrile ($\epsilon = 36.6$). The low energy transitions at $\sim 665 \text{ nm}$ show little variation as a function of solvent polarity (Figure 2b) since this band is attributable to transitions between states involving the HOMO and LUMO of $3\text{H}(\text{Phl}^{\text{CF}_3})$, and these frontier orbitals are not appreciably polarized.

Additional photophysical measurements recorded for $3\text{H}(\text{Phl}^{\text{CF}_3})$ revealed that this phlorin is weakly emissive with a fluorescence quantum yield of $\Phi_{\text{Fl}} = 5.70 \times 10^{-4}$ and associated excited-state lifetime of $\tau_{\text{Fl}} = 45 \text{ ps}$ in deaerated CH_2Cl_2 . Both these values are in line with those observed for other electron deficient phlorin derivatives.³⁶

Many polypyrrole platforms display a pronounced supramolecular chemistry via formation of hydrogen bonds between the pyrrole N–H moieties and fluoride.^{29,30,54–56} Titration of CH_2Cl_2 solutions of $3\text{H}(\text{Phl}^{\text{CF}_3})$ with aliquots of TBAF is accompanied by the spectral changes shown in Figure S2a, Supporting Information. Well-anchored isosbestic points are maintained during the course of the TBAF titration, suggesting

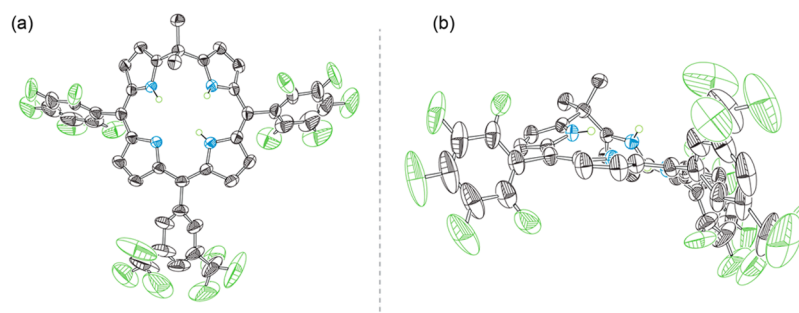


Figure 1. Solid-state structure of **3H(Phl^{CF₃})** shown from (a) above the plane of the macrocycle and (b) side on. All non-nitrogen-bound hydrogen atoms have been omitted for clarity. Atom ellipsoids shown at 50% probability.

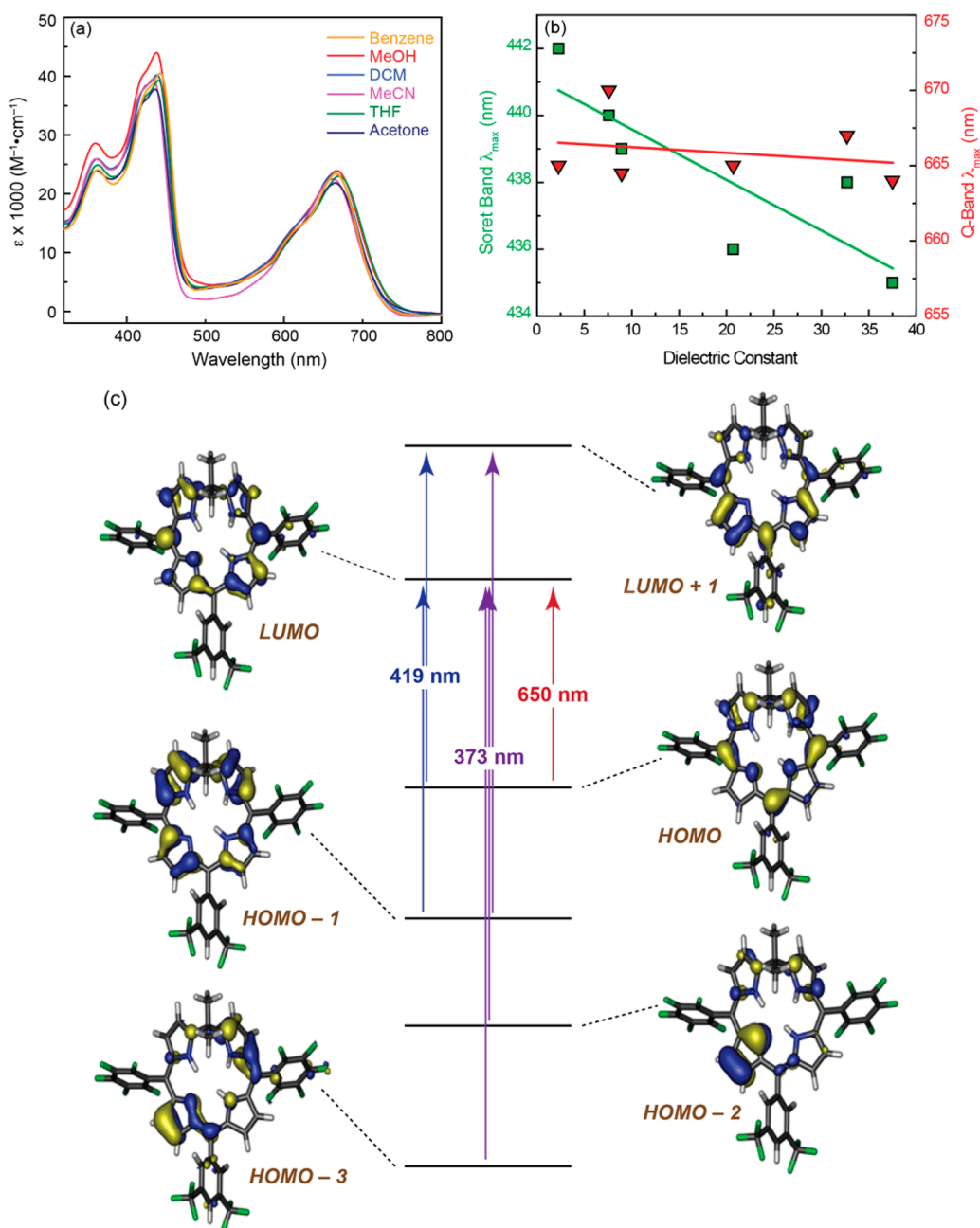


Figure 2. (a) Absorbance spectra recorded for **3H(Phl^{CF₃})** in solvents of varying polarity. (b) Extent to which solvent polarity perturbs λ_{max} of the Soret and Q-bands for **3H(Phl^{CF₃})**. (c) Representation of the molecular orbitals involved in the major Soret and Q-band transitions.

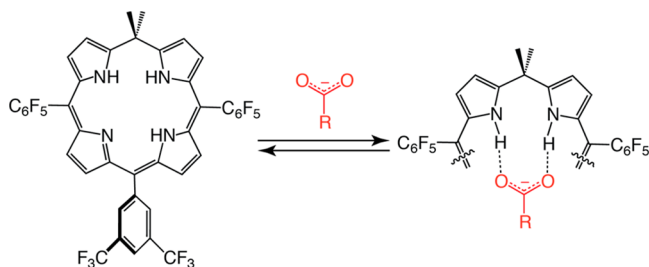
a direct conversion of freebase phlorin to the fluoride bound species. As has been observed for other phlorin architectures,^{34,36,57} Job analysis showed that $3\text{H}(\text{Phl}^{\text{CF}_3})$ is capable of binding up to two equivalents of F^- to form $3\text{H}(\text{Phl}^{\text{CF}_3})\cdot 2\text{F}^-$ (Figure S2b, Supporting Information). Moreover, binding of F^- to this phlorin is highly cooperative, as a Hill analysis (Figure S2c, Supporting Information) of the titration data produced a well-fit linear regression, which yields a cooperativity constant of $\beta_2 = 1.6 \times 10^{13} \text{ M}^{-2}$ in CH_2Cl_2 .

Binding of F^- to $3\text{H}(\text{Phl}^{\text{CF}_3})$ is very strong and persists in polar aprotic solvents. Titration of $3\text{H}(\text{Phl}^{\text{CF}_3})$ in MeCN with TBAF leads to similar spectral changes in the visible and near-IR regions to those observed in CH_2Cl_2 (Figure S3a, Supporting Information). While Job and Hill analyses (Figure S3, Supporting Information) revealed that F^- binding is cooperative in MeCN, the termolecular association constant is reduced to $\beta_2 = 6.4 \times 10^5 \text{ M}^{-2}$ in this more polar solvent.

The observation that fluoride binding to $3\text{H}(\text{Phl}^{\text{CF}_3})$ is still rapid and highly cooperative in a solvent as polar as MeCN is notable, as hydrogen-bonding of halides to the pyrrole N–H groups of porphyrinoids is typically only observed in less polar solvents such as THF and CH_2Cl_2 . We note that based on similar UV–vis titration experiments, $3\text{H}(\text{Phl}^{\text{CF}_3})$ does not bind less basic halides such as Cl^- or Br^- . That fluoride is the only halide to associate via hydrogen-bonding to the phlorin N–H residues suggesting that the strength of this host–guest interaction may be sensitive to the anion's size and/or basicity.

In order to shed light on the factors that drive anion association with the phlorin scaffold, we sought a hydrogen-bond acceptor for which the steric properties and acidity could be independently varied. On the basis of the physical structure of $3\text{H}(\text{Phl}^{\text{CF}_3})$, we hypothesized that the phlorin would be an excellent receptor for carboxylate anions via formation of a two point hydrogen-bond between the carboxylate oxygen atoms and the pyrrole N–H residues on the side of the phlorin bearing the 5,5-dimethyl substituents (Scheme 2). Noting that some expanded and reduced polypyrrole macrocycles can bind oxygen anions,^{54,58} we set out to determine if a similar supramolecular chemistry exists for $3\text{H}(\text{Phl}^{\text{CF}_3})$.

Scheme 2. Binding of Carboxylate Guests by a 5,5-Dimethyl Phlorin Architecture^a



^aNote: The bottom half of $3\text{H}(\text{Phl}^{\text{CF}_3})$ and the bis-trifluoromethyl-phenyl substituent at the 15-position of the phlorin macrocycle has been omitted for clarity.

A solution of $3\text{H}(\text{Phl}^{\text{CF}_3})$ in MeCN was titrated with tetrabutylammonium acetate (TBAOAc), which produced a series of spectral shifts across the UV–vis and near-IR regions (Figure 3a) that are similar to those observed for the TBAF titrations (vide supra). The magnitude and intensity of these spectral shifts are much larger than those observed upon binding of carboxylates and other anions to porphyrinoids

bearing protonic functionalities that are conjugated along the periphery of the chromophore π -system.^{59–61}

In contrast to the fluoride binding experiments described above, Job analysis conducted for association of TBAOAc to $3\text{H}(\text{Phl}^{\text{CF}_3})$ showed that the phlorin only binds one equivalent of acetate to form $3\text{H}(\text{Phl}^{\text{CF}_3})\cdot\text{OAc}^-$ (Figure 3b). Consistent with this 1:1 binding model, Benesi–Hildebrand fitting of this titration data produced a well-fit linear regression (Figure 3a, inset) yielding a formation constant of $K_f = 440$ for $3\text{H}(\text{Phl}^{\text{CF}_3})\cdot\text{OAc}^-$. These experiments represent the first demonstration that carboxylates can hydrogen-bond to the phlorin architecture. Moreover, the observation that $3\text{H}(\text{Phl}^{\text{CF}_3})\cdot\text{OAc}^-$ forms in a significantly polar solvent such as MeCN speaks to the strength of this hydrogen-bonding interaction. The magnitude of the association constant for $3\text{H}(\text{Phl}^{\text{CF}_3})\cdot\text{OAc}^-$ in MeCN is similar to that observed for formation of amidinium-carboxylate hydrogen bonding networks.^{61–63} Despite the appreciable formation constant for $3\text{H}(\text{Phl}^{\text{CF}_3})\cdot\text{OAc}^-$, we note that binding of acetate to the phlorin N–H residues is completely reversible; the addition of small amounts of polar protic solvents such as MeOH to MeCN solutions of $3\text{H}(\text{Phl}^{\text{CF}_3})\cdot\text{OAc}^-$ disrupts these hydrogen-bonded assemblies, as evidenced by reversion of the UV–vis profile to that of uncomplexed $3\text{H}(\text{Phl}^{\text{CF}_3})$ (Figure S4, Supporting Information).

To determine the extent to which the carboxylate anion's size impacts its ability to bind to the phlorin, we repeated the titration experiment shown in Figure 3 using 4-dimethylaminobenzoate (3) as the hydrogen-bond acceptor. This carboxylate is significantly larger than acetate but, as shown in Table 1, has a $\text{p}K_a$ in MeCN that is very close in value to its smaller homologue ($\text{p}K_a$ of $\text{OAc}^- = 22.3$; $\text{p}K_a$ of 3 = 23.0).⁶⁴ Analysis of the binding data obtained upon titration of $3\text{H}(\text{Phl}^{\text{CF}_3})$ with 3 reveals that the hydrogen-bonded assembly $3\text{H}(\text{Phl}^{\text{CF}_3})\cdot 3$ forms with a formation constant of $K_f = 435$. This titration experiment not only confirms that larger anions can bind to $3\text{H}(\text{Phl}^{\text{CF}_3})$ but also indicates that carboxylate anions of similar basicity but disparate size bind to the phlorin to near equal extents. These results suggest that the larger halides such as Cl^- or Br^- should be able to associate with the phlorin based purely on sterics and that the lack of hydrogen-bonding observed for halides larger than F^- is due to the decreased basicity of these anions ($\text{p}K_a$ values for HF, HCl, and HBr in aprotic polar solvent are ~ 15 , 1.8, and 0.9, respectively).⁶⁵

The effect that anion basicity holds for formation of supramolecular phlorin assemblies was further probed by screening the ability of other carboxylates to hydrogen-bond to the pyrrole N–H residues of $3\text{H}(\text{Phl}^{\text{CF}_3})$. In addition to 4-dimethylaminobenzoate (3), we surveyed the TBA salts of benzoate (4), 4-bromobenzoate (5), and 4-nitrobenzoate (6). Job and Benesi–Hildebrand analysis of the UV–vis spectral shifts observed upon association of these anions with $3\text{H}(\text{Phl}^{\text{CF}_3})$ showed that each of the carboxylates form 1:1 adducts with the phlorin macrocycle. Table 1 summarizes the formation constants (K_f) for the corresponding 1:1 hydrogen-bonded $3\text{H}(\text{Phl}^{\text{CF}_3})$ assemblies in MeCN, along with the corresponding $\text{p}K_a$ values for each of the carboxylates studied.⁶⁴ This data clearly shows that the stability of the hydrogen bonded adducts is well correlated with the basicity of the carboxylate anions. We note that carboxylates that are more acidic than 4-nitrobenzoate do not form supramolecular assemblies with $3\text{H}(\text{Phl}^{\text{CF}_3})$ in MeCN. For instance, the

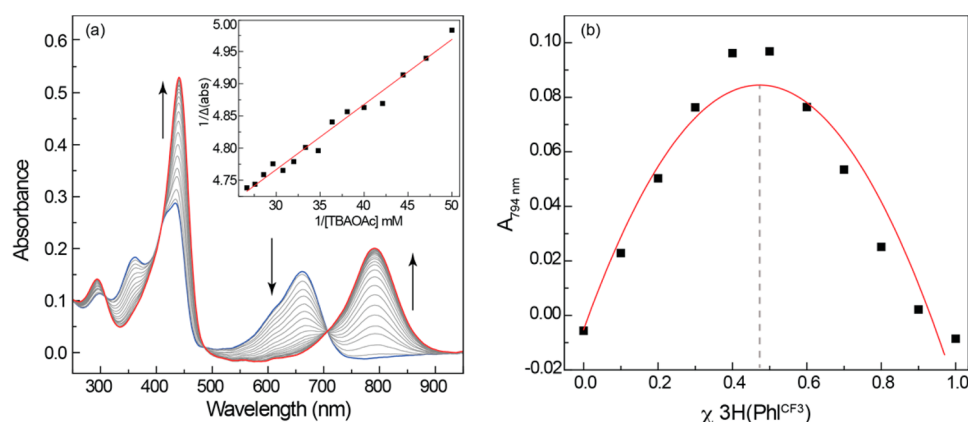


Figure 3. (a) Changes in the UV-vis absorbance spectrum of $3\text{H}(\text{Phl}^{\text{CF}_3})$ upon titration with TBAOAc. Inset: Benesi-Hildebrand plot constructed for OAc^- binding to generate $3\text{H}(\text{Phl}^{\text{CF}_3})\cdot\text{OAc}^-$. (b) Job plot constructed for titration of $3\text{H}(\text{Phl}^{\text{CF}_3})$ with TBAOAc in MeCN.

Table 1. Thermodynamic Parameters for Binding of Carboxylates to $3\text{H}(\text{Phl}^{\text{CF}_3})$ in MeCN

anion	anion pK_a^a	1:1 assembly	K_f
OAc^-	22.3	$3\text{H}(\text{Phl}^{\text{CF}_3})\cdot\text{OAc}^-$	440
4-Me ₂ - ϕ - CO_2^- (3)	23.0	$3\text{H}(\text{Phl}^{\text{CF}_3})\cdot 3$	435
PhCO_2^- (4)	20.7	$3\text{H}(\text{Phl}^{\text{CF}_3})\cdot 4$	27.0
4-Br- ϕ - CO_2^- (5)	20.3	$3\text{H}(\text{Phl}^{\text{CF}_3})\cdot 5$	8.21
4-O ₂ N- ϕ - CO_2^- (6)	18.7	$3\text{H}(\text{Phl}^{\text{CF}_3})\cdot 6$	1.79

^a pK_a values correspond to the conjugate acid of the anions listed and are reported in MeCN as reproduced from ref 64.

addition of up to 3500 equiv of tetrabutylammonium 3,5-dinitrobenzoate ($\text{pK}_a = 17.0$ in MeCN)⁶⁴ to a solution of phlorin did not alter the absorption spectrum of the MeCN solution. Although it is possible that steric interaction between the anion guest and phlorin macrocycle also impact formation of the supramolecular assemblies described above, we note that the addition of small, weakly coordinating anions such as methanesulfonate, perchlorate, or nitrate to MeCN solutions of $3\text{H}(\text{Phl}^{\text{CF}_3})$ does not result in formation of hydrogen-bonded assemblies as judged by UV-vis spectroscopy.

Phlorins display a rich redox chemistry, which can also be tuned via hydrogen-bonding of anions to the phlorin core. Differential pulse voltammetry (DPV) was utilized to study the redox behavior of $3\text{H}(\text{Phl}^{\text{CF}_3})$ as this electrochemical technique offers higher sensitivity than more conventional cyclic voltammetry measurements for analysis of samples with low analyte concentrations.⁶⁶ DPV experiments recorded for a 1.0 mM solution of $3\text{H}(\text{Phl}^{\text{CF}_3})$ in MeCN containing 0.1 M TBAPF₆ showed that this porphyrinoid can be oxidized by up to three electrons. The DPV trace recorded for this phlorin (Figure 4, blue trace) shows oxidation waves at $E_{\text{ox}}(1) = 0.42$ V, $E_{\text{ox}}(2) = 0.67$ V, and $E_{\text{ox}}(3) = 0.79$ V versus Ag/AgCl. These values are in line with those observed for other electron deficient phlorins.³⁶ Just as hydrogen-bonding to the N-H groups of $3\text{H}(\text{Phl}^{\text{CF}_3})$ perturbs the phlorin spectral properties, the addition of either F^- or OAc^- to an MeCN solution of $3\text{H}(\text{Phl}^{\text{CF}_3})$ dramatically alters the phlorin redox properties. Formation of the F^- and OAc^- bound adducts ($3\text{H}(\text{Phl}^{\text{CF}_3})\cdot 2\text{F}^-$ and $3\text{H}(\text{Phl}^{\text{CF}_3})\cdot\text{OAc}^-$, respectively) shifts all three phlorin oxidation waves to less positive potentials, which is expected upon going from the neutral phlorin to the negatively charged fluoride and acetate adducts. This potential shift is also consistent with raising the energy of the phlorin HOMO and

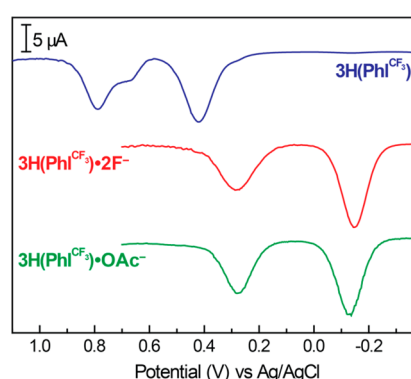


Figure 4. Differential pulse voltammetry (DPV) traces recorded for $3\text{H}(\text{Phl}^{\text{CF}_3})$ (blue), $3\text{H}(\text{Phl}^{\text{CF}_3})\cdot 2\text{F}^-$ (red), and $3\text{H}(\text{Phl}^{\text{CF}_3})\cdot\text{OAc}^-$ (green) in MeCN containing 0.1 M TBAPF₆.

is mirrored by the bathochromic shift observed for in the UV-vis absorbance spectrum upon binding of anions to $3\text{H}(\text{Phl}^{\text{CF}_3})$ (vide supra). In contrast to the electrochemical response observed upon binding of F^- to phlorins in CH_2Cl_2 ,³⁶ association of F^- or OAc^- with $3\text{H}(\text{Phl}^{\text{CF}_3})$ in MeCN causes the first and second oxidation waves to coalesce into a two electron wave ($E_{\text{ox}} = -0.14$ and -0.13 V for $3\text{H}(\text{Phl}^{\text{CF}_3})\cdot 2\text{F}^-$ and $3\text{H}(\text{Phl}^{\text{CF}_3})\cdot\text{OAc}^-$, respectively). Both these supramolecular assemblies can also be oxidized by a third electron at ~ 0.28 V.

SUMMARY AND FUTURE DIRECTIONS

In summary, we have prepared a new 5,5-dimethylphlorin porphyrinoid. Unlike conventional porphyrins, this phlorin is significantly distorted from planarity and displays solvatochromism in the Soret region due to the polarized nature of the frontier orbital (LUMO+1) involved in the major electronic transitions clustered around ~ 370 – 420 nm. Compound $3\text{H}(\text{Phl}^{\text{CF}_3})$ displays an intriguing supramolecular chemistry with sufficiently basic anions, as this phlorin can cooperatively hydrogen-bond to two equivalents of F^- to form $3\text{H}(\text{Phl}^{\text{CF}_3})\cdot 2\text{F}^-$. Binding of fluoride to the N-H residues of $3\text{H}(\text{Phl}^{\text{CF}_3})$ is manifest in significant perturbation to the phlorin's electronic structure and drives significant changes to the phlorin's photophysical and redox properties.

Although $3\text{H}(\text{Phl}^{\text{CF}_3})$ is a selective receptor for fluoride over larger halides (i.e., Cl^- and Br^-), this porphyrinoid does support a robust supramolecular chemistry with other anions.

In this work, we have demonstrated, for the first time, that the phlorin framework is capable of binding carboxylate anions. Unlike the stoichiometry observed for the fluoride binding experiments, $3\text{H}(\text{Phl}^{\text{CF}_3})$ can reversibly hydrogen-bond to one equivalent of a suitably basic carboxylate. Although the binding of carboxylates to the phlorin framework is not cooperative, it is difficult to make direct comparisons between these two supramolecular phenomena. Nonetheless, distinct similarities observed upon association of carboxylates to the phlorin core, as formation of supramolecular assemblies such as $3\text{H}(\text{Phl}^{\text{CF}_3})\cdot\text{OAc}^-$ is manifest in comparable shifts to the phlorin UV–vis absorbance and redox properties to those observed upon fluoride binding. Association of fluoride and/or carboxylates with $3\text{H}(\text{Phl}^{\text{CF}_3})$ is observed in relatively polar solvents such as MeCN, which attests to the strength of the hydrogen-bonding interactions that drive formation of these supramolecular assemblies.

The ability to independently vary the size and $\text{p}K_{\text{a}}$ of a series of carboxylates has also allowed us to probe how phlorin-anion association is influenced by the anion's size and/or basicity. By assessing the extent to which a series of carboxylates form hydrogen-bonded assemblies with the phlorin, we have demonstrated that only carboxylates that are more electron-rich than 4-nitrobenzoate form supramolecular assemblies with $3\text{H}(\text{Phl}^{\text{CF}_3})$ to an appreciable extent in MeCN.

Furthermore, small anion guests such as nitrite and mesylate, which should be able to bind to the phlorin N–H residues based solely on steric constraints, do not form supramolecular assemblies with $3\text{H}(\text{Phl}^{\text{CF}_3})$ as judged by UV–vis spectroscopy. Further, these experiments clearly show that carboxylate guests of similar basicity but disparate size bind to the phlorin host with near identical association constants. When taken together, these results suggest that the phlorin can selectively recognize fluoride over other halogens due to the dramatic drop in $\text{p}K_{\text{a}}$ of the hydrohalic acids as one descends group 17 of the periodic table. The improved understanding of the factors that control hydrogen-bonding and anion recognition by the phlorin platform, which has been garnered by these studies, should aid the development of new detection schemes for fluoride and other sufficiently basic anions.

■ ASSOCIATED CONTENT

Supporting Information

Synthetic protocols and spectroscopic, crystallographic, and computational data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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■ REFERENCES

- (1) Wang, Q.; Campbell, W. M.; Bonfantani, E. E.; Jolley, K. W.; Officer, D. L.; Walsh, J.; et al. Efficient Light Harvesting by Using Green Zn-Porphyrin-Sensitized Nanocrystalline TiO_2 Films. *J. Phys. Chem. B* **2005**, *109*, 15397–15409.
- (2) Gust, D.; Moore, T. A.; Moore, A. L. Mimicking Photosynthetic Solar Energy Transduction. *Acc. Chem. Res.* **2001**, *34*, 40–48.
- (3) Campbell, W. M.; Burrell, A. K.; Officer, D. L.; Jolley, K. W. Porphyrins as Light Harvesters in the Dye-Sensitized TiO_2 Solar Cell. *Coord. Chem. Rev.* **2004**, *248*, 1363–1379.
- (4) Kay, A.; Graetzel, M. Artificial Photosynthesis. 1. Photosensitization of Titania Solar Cells with Chlorophyll Derivatives and Related Natural Porphyrins. *J. Phys. Chem.* **1993**, *97*, 6272–6277.
- (5) Kay, A.; Humphry-Baker, R.; Graetzel, M. Artificial Photosynthesis. 2. Investigations on the Mechanism of Photosensitization of Nanocrystalline TiO_2 Solar Cells by Chlorophyll Derivatives. *J. Phys. Chem.* **1994**, *98*, 952–959.
- (6) Campbell, W. M.; Jolley, K. W.; Wagner, P.; Wagner, K.; Walsh, P. J.; Gordon, K. C.; et al. Highly Efficient Porphyrin Sensitizers for Dye-Sensitized Solar Cells. *J. Phys. Chem. C* **2007**, *111*, 11760–11762.
- (7) Yella, A.; Lee, H.-W.; Tsao, H. N.; Yi, C.; Chandiran, A. K.; Nazeeruddin, M. K.; et al. Porphyrin-Sensitized Solar Cells with Cobalt (II/III)-Based Redox Electrolyte Exceed 12% Efficiency. *Science* **2011**, *334*, 629–634.
- (8) Wheeler, B. L.; Nagasubramanian, G.; Bard, A. J.; Schechtman, L. A.; Kenney, M. E. A Silicon Phthalocyanine and a Silicon Naphthalocyanine: Synthesis, Electrochemistry, and Electrogenenerated Chemiluminescence. *J. Am. Chem. Soc.* **1984**, *106*, 7404–7410.
- (9) Tokel, N. E.; Keszthelyi, C. P.; Bard, A. J. Electrogenenerated Chemiluminescence. X. $\alpha,\beta,\gamma,\delta$ -Tetraphenylporphine Chemiluminescence. *J. Am. Chem. Soc.* **1972**, *94*, 4872–4877.
- (10) Long, T. R.; Richter, M. M. Electrogenenerated Chemiluminescence of the Platinum (II) Octaethylporphyrin/Tri-*n*-propylamine System. *Inorg. Chim. Acta* **2005**, *358*, 2141–2145.
- (11) Saji, T.; Bard, A. J. Electrogenenerated Chemiluminescence. 29. The Electrochemistry and Chemiluminescence of Chlorophyll *a* in *N,N*-Dimethylformamide Solutions. *J. Am. Chem. Soc.* **1977**, *99*, 2235–2240.
- (12) Soombar, C.; Troiani, V.; Bruno, C.; Marcaccio, M.; Paolucci, F.; Listorti, A.; Belbarkra, A.; Amramaroli, N.; Magistrato, A.; De Zorzi, R.; Bonifazi, D. Synthesis, Photophysical, Electrochemical, and Electrochemiluminescent Properties of 5,15-Bis(9-anthracenyl)-porphyrin Derivatives. *Org. Biomol. Chem.* **2009**, *7*, 2402–2413.
- (13) Wu, L.; Wang, J.; Feng, L.; Ren, J.; Wei, W.; Qu, X. Label-Free Ultrasensitive Detection of Human Telomerase Activity Using Porphyrin-Functionalized Graphene and Electrochemiluminescence Technique. *Adv. Mater.* **2012**, *24*, 2447–2452.
- (14) Bolin, A.; Richter, M. M. Coreactant Electrogenenerated Chemiluminescence of Ruthenium Porphyrins. *Inorg. Chim. Acta* **2009**, *362*, 1974–1976.
- (15) Chen, F.-C.; Ho, J.-H.; Chen, C.-Y.; Su, Y. O.; Ho, T.-I. Electrogenenerated Chemiluminescence of Sterically Hindered Porphyrins in Aqueous Media. *J. Electroanal. Chem.* **2001**, *499*, 17–23.
- (16) Rosenthal, J.; Nepomnyashchii, A. B.; Kozhukh, J.; Bard, A. J.; Lippard, S. J. Synthesis, Photophysics, Electrochemistry, and Electrogenenerated Chemiluminescence of a Homologous Set of BODIPY-Appended Bipyridine Derivatives. *J. Phys. Chem. C* **2011**, *115*, 17993–18001.

- (17) Nepomnyashchii, A. B.; Pistner, A. J.; Bard, A. J.; Rosenthal, J. Synthesis, Photophysics, Electrochemistry and Electrogenerated Chemiluminescence of PEG-Modified BODIPY Dyes in Organic and Aqueous Solutions. *J. Phys. Chem. C* **2013**, *117*, 5599–5609.
- (18) Qi, H.; Teesdale, J. J.; Pupillo, R. C.; Rosenthal, J.; Bard, A. J. Synthesis, Electrochemistry, and Electrogenerated Chemiluminescence of Two BODIPY-Appended Bipyridine Homologues. *J. Am. Chem. Soc.* **2013**, *135*, 13558–13566.
- (19) Nepomnyashchii, A. B.; Bard, A. J. Electrochemistry and Electrogenerated Chemiluminescence of BODIPY Dyes. *Acc. Chem. Res.* **2012**, *45*, 1844–1853.
- (20) Floriani, C.; Floriani-Moro, R. In *The Porphyrin Handbook*; Kadish, K. M., Smith, K. M., Guillard, R., Eds.; Academic Press: New York, 2000.
- (21) Harel, Y.; Manassen, J. Hydrogen Transfer Photocatalyzed by Metalloporphyrins in Visible Light. Photoinduced Redox Cycling of the Catalyst. *J. Am. Chem. Soc.* **1977**, *99*, 5817–5818.
- (22) Kalyanasundaram, K.; Gratzel, M. Light Induced Redox Reactions of Water Soluble Porphyrins, Sensitization of Hydrogen Generation from Water by Zincporphyrin Derivatives. *Helv. Chim. Acta* **1980**, *63*, 478–485.
- (23) Bartocci, C.; Maldotti, A.; Varani, G.; Battioni, P.; Carassiti, V.; Mansuy, D. Photoredox and Photocatalytic Characteristics of Various Iron Meso-Tetraarylporphyrins. *Inorg. Chem.* **1991**, *30*, 1255–1259.
- (24) Rosenthal, J.; Pistorio, B.; Chng, L.; Nocera, D. G. Aerobic Catalytic Photooxidation of Olefins by an Electron-Deficient Pacman Bisiron(III) μ -Oxo Porphyrin. *J. Org. Chem.* **2005**, *70*, 1885–1888.
- (25) Rosenthal, J.; Luckett, T. D.; Hodgkiss, J. M.; Nocera, D. G. Photocatalytic Oxidation of Hydrocarbons by a Bis-iron(III)- μ -oxo Pacman Porphyrin Using O_2 and Visible Light. *J. Am. Chem. Soc.* **2006**, *128*, 6546–6547.
- (26) Korobkov, I.; Gambarotta, S.; Yap, G. P. A. A Highly Reactive Uranium Complex Supported by the Calix[4]tetrapyrrole Tetraanion Affording Dinitrogen Cleavage, Solvent Deoxygenation, and Polysilanol Depolymerization. *Angew. Chem., Int. Ed.* **2002**, *41*, 3433–3436.
- (27) Harmjanz, M.; Gill, H. S.; Scott, M. J. Porphodimethene–Porphyrin Interconversion: A Tetrapyrrolic Redox-Switchable Macrocycle. *J. Am. Chem. Soc.* **2000**, *122*, 10476–10477.
- (28) Harmjanz, M.; Scott, M. J. Facile Synthesis of Stacked, Heteronuclear Porphyrin Arrays with Varied Architectures. *Inorg. Chem.* **2000**, *39*, 5428–5429.
- (29) Gale, P. A.; Sessler, J. L.; Král, V.; Lynch, V. Calix[4]pyrroles: Old Yet New Anion-Binding Agents. *J. Am. Chem. Soc.* **1996**, *118*, 5140–5141.
- (30) Gale, P. A.; Anzenbacher, P., Jr.; Sessler, J. L. Calixpyrroles II. *Coord. Chem. Rev.* **2001**, *222*, 57–102.
- (31) Bachmann, J.; Nocera, D. G. Multielectron Chemistry of Zinc Porphyrinogen: A Ligand-Based Platform for Two-Electron Mixed Valency. *J. Am. Chem. Soc.* **2004**, *126*, 2829–2837.
- (32) Bachmann, J.; Nocera, D. G. Multielectron Redox Chemistry of Iron Porphyrinogens. *J. Am. Chem. Soc.* **2005**, *127*, 4730–4743.
- (33) Bachmann, J.; Teets, T. S.; Nocera, D. G. Proton Storage in the Periphery of Zirconium(IV) Porphyrinogen. *Dalton Trans.* **2008**, *34*, 4549–4551.
- (34) Pistner, A. J.; Yap, G. P. A.; Rosenthal, J. A Tetrapyrrole Macrocycle Displaying a Multielectron Redox Chemistry and Tunable Absorbance Profile. *J. Phys. Chem. C* **2012**, *116*, 16918–16924.
- (35) Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. Safe and Convenient Procedure for Solvent Purification. *Organometallics* **1996**, *15*, 1518–1520.
- (36) Pistner, A. J.; Lutterman, D. A.; Ghidui, M. J.; Ma, Y.-Z.; Rosenthal, J. Synthesis, Electrochemistry, and Photophysics of a Family of Phlorin Macrocycles That Display Cooperative Fluoride Binding. *J. Am. Chem. Soc.* **2013**, *135*, 6601–6607.
- (37) Brouwer, A. M. Standards for Photoluminescence Quantum Yield Measurements in Solution. *Pure Appl. Chem.* **2011**, *83*, 2213–2228.
- (38) Calvert, J. M.; Caspar, J. V.; Binstead, R. A.; Westmoreland, T. D.; Meyer, T. J. Metallopolymer Photochemistry. Photophysical, Photochemical and Photoelectrochemical Properties of $(bpy)_2Ru^{II}$ Sites Bound to Poly(4-vinylpyridine). *J. Am. Chem. Soc.* **1982**, *104*, 6620–6627.
- (39) Ma, Y.; Shaw, R.; Yu, X.; O’Neil, H. M.; Hong, K. Excited-State Dynamics of Water-Soluble Polythiophene Derivatives: Temperature and Side-Chain Length Effects. *J. Phys. Chem. B* **2012**, *116*, 14451–14460.
- (40) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; et al. *Gaussian 09*, revision A.1; Gaussian, Inc., Wallingford, CT, 2009.
- (41) Becke, A. D. Density-Functional Thermochemistry. III. The Role of Exact Exchange. *J. Chem. Phys.* **1993**, *98*, 5648–5652.
- (42) Becke, A. D. Density-Functional Exchange-Energy Approximation with Correct Asymptotic Behavior. *Phys. Rev. A* **1988**, *38*, 3098–3100.
- (43) Lee, C.; Yang, W.; Parr, R. G. Development of the Colle–Salvetti Correlation-Energy Formula into a Functional of the Electron Density. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1988**, *37*, 785–789.
- (44) Cancès, M. T.; Mennucci, B.; Tomasi, J. A New Integral Equation Formalism for the Polarizable Continuum Model: Theoretical Background and Applications to Isotropic and Anisotropic Dielectrics. *J. Chem. Phys.* **1997**, *107*, 3032–3041.
- (45) Tomasi, J.; Persico, M. Molecular Interactions in Solution: An Overview of Methods Based on Continuous Distributions of the Solvent. *Chem. Rev.* **1994**, *94*, 2027–2094.
- (46) Cossi, M.; Barone, V.; Mennucci, B.; Tomasi, J. Ab Initio Study of Ionic Solutions by a Polarizable Continuum Dielectric Model. *Chem. Phys. Lett.* **1998**, *286*, 253–260.
- (47) Mennucci, B.; Tomasi, J. Continuum Solvation Models: A New Approach to the Problem of Solute’s Charge Distribution and Cavity Boundaries. *J. Chem. Phys.* **1997**, *106*, 5151–5158.
- (48) Cossi, M.; Scalmani, G.; Rega, N.; Barone, V. New Developments in the Polarizable Continuum Model for Quantum Mechanical and Classical Calculations on Molecules in Solution. *J. Chem. Phys.* **2002**, *117*, 43–54.
- (49) O’Brien, A. Y.; McGann, J. P.; Geier, G. R. Dipyrromethane + Dipyrromethanedicarbinol Routes to an Electron Deficient Meso-Substituted Phlorin with Enhanced Stability. *J. Org. Chem.* **2007**, *72*, 4084–4092.
- (50) Gouterman, M. Study of the Effects of Substitution on the Absorption Spectra of Porphin. *J. Chem. Phys.* **1959**, *30*, 1139–1161.
- (51) Gouterman, M. Spectra of Porphyrins. *J. Mol. Spectrosc.* **1961**, *6*, 138–163.
- (52) Gouterman, M.; Wagnière, G. H. Spectra of Porphyrins: Part II. Four Orbital Model. *J. Mol. Spectrosc.* **1963**, *11*, 108–127.
- (53) Spellane, P. J.; Gouterman, M.; Antipas, A.; Kim, S.; Liu, Y. C. Porphyrins. 40. Electronic Spectra and Four-Orbital Energies of Free-Base, Zinc, Copper, and Palladium Tetrakis(perfluorophenyl)-porphyrins. *Inorg. Chem.* **1980**, *19*, 386–391.
- (54) Sessler, J. L.; Cyr, M.; Furuta, H.; Král, V.; Mody, T.; Morishima, T.; Shionoya, M.; Weghorn, S. Anion Binding: A New Direction in Porphyrin-Related Research. *Pure Appl. Chem.* **1993**, *65*, 393–398.
- (55) Král, V.; Sessler, J. L.; Zimmerman, R. S.; Seidel, D.; Lynch, V.; Andrioletti, B. Calixphyrins: Novel Macrocycles at the Intersection between Porphyrins and Calixpyrroles. *Angew. Chem., Int. Ed.* **2000**, *39*, 1055–1058.
- (56) Sessler, J. L.; Zimmerman, R. S.; Bucher, C.; Král, V.; Andrioletti, B. Calixphyrins. Hybrid Macrocycles at the Structural Crossroads between Porphyrins and Calixpyrroles. *Pure Appl. Chem.* **2001**, *73*, 1041–1057.
- (57) Ka, J.-W.; Lee, C.-H. Unusual Phlorins from the Oxidative Coupling of Pentapyrromethanes: Their Facile Conversion to meso-Substituted Porphyrins. *Tetrahedron Lett.* **2001**, *42*, 4527–4529.
- (58) Sessler, J. L.; Hoehner, M. C.; Gebauer, A.; Andrievsky, A.; Lynch, V. Synthesis and Characterization of All-Alkyl-Substituted Mono-, Di-, and Trioxasapphyrins. *J. Org. Chem.* **1997**, *62*, 9251–9260.

- (59) Rosenthal, J.; Hodgkiss, J. M.; Young, E. R.; Nocera, D. G. Spectroscopic Determination of Proton Position in the Proton-Coupled Electron Transfer Pathways of Donor–Acceptor Supramolecule Assemblies. *J. Am. Chem. Soc.* **2006**, *128*, 10474–10483.
- (60) Rosenthal, J.; Young, E. R.; Nocera, D. G. Structurally Homologous β - and meso-Alkynyl Amidinium Porphyrins. *Inorg. Chem.* **2007**, *46*, 8668–8675.
- (61) Young, E. R.; Rosenthal, J.; Nocera, D. G. Spectral Observation of Conversion between Ionized vs. Non-ionized Proton-Coupled Electron Transfer Interfaces. *Chem. Commun.* **2008**, 2322–2324.
- (62) Jorgenson, W. L.; Pranata, J. Importance of Secondary Interactions in Triply Hydrogen Bonded Complexes: Guanine-Cytosine vs Uracil-2,6-Diaminopyridine. *J. Am. Chem. Soc.* **1990**, *112*, 2008–2010.
- (63) Pranata, J.; Wierschke, S. G.; Jorgensen, W. L. OPLS Potential Functions for Nucleotide Bases. Relative Association Constants of Hydrogen-Bonded Base Pairs in Chloroform. *J. Am. Chem. Soc.* **1991**, *113*, 2810–2819.
- (64) Izutsu, K. *Acid–Base Dissociation Constants in Dipolar Aprotic Solvents*; Blackwell Scientific: Cambridge, MA, 1990.
- (65) Bordwell, F. G. Equilibrium Acidities in Dimethyl Sulfoxide Solution. *Acc. Chem. Res.* **1988**, *21*, 456–463.
- (66) Bard, A. J.; Faulkner, L. R. *Electrochemical Methods: Fundamentals and Applications*; John Wiley: New York, 1980.