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

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ABSTRACT: A new 5,5-dimethylphlorin derivative (3H-Phl$^{CF_3}$) 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$^{CF_3}$) also displays an intriguing supramolecular chemistry with certain anions; this phlorin can cooperatively hydrogen-bond two equivalents of fluoride to form 3H(Phl$^{CF_3}$)-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$^{CF_3}$)-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 pKₐ 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,1–17 electrogenerated chemiluminescence,8–19 and photocatalysis.20–25 Additionally, tetrapyrrole macrocycles, such as porphyrinogens and related complexes that contain sp$^3$ hybridized meso-carbons,26–28 can support an intriguing supramolecular chemistry with anions29,30 and multielectron redox properties31,32 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 sp$^3$ 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 sp$^3$ 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...
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 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)pyrromethane (1) was prepared using a previously published method.36 The synthesis of 2 and 3H(PhlCF₃) 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 conducted by placing 2.0 mL of 10 μM solutions of 3H(PhlCF₃) 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(PhlCF₃), 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(PhlCF₃) was carried out using solutions containing 10 μM of total analyte (TBAF + 3H(PhlCF₃)). The ratio of 3H(PhlCF₃) 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(PhlCF₃) 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(PhlCF₃) 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 (Φₑ = 0.27) as the reference actinometer using the expression below,38

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Φₑ = \Phiₑ = \frac{Aₑ}{Aₑ} \left( \frac{Iₑ}{Iₑ} \right) \left( \frac{ηₑ}{ηₑ} \right) \]

where Φₑ and Φₑ are the emission quantum yield of the sample and the reference, respectively, and are the measured absorbance of the reference and sample at the excitation wavelength, respectively, and and are the integrated emission intensities of the reference and sample, respectively, and and 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 ($\chi^2$) value is used to judge the quality of each fit.

**X-ray Crystallography.** Crystals of 3H(Phl(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–Kα radiation ($\lambda = 0.71073$ Å). Unit cell parameters were obtained from 36 data frames, 0.3°/ω, 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 reabsorption corrections based on redundant multiscan data. 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 reabsorption corrections based on redundant multiscan data.

**Computations.** All density functional calculations were performed using the Gaussian 09 (G09) program package, with the Becke three-parameter hybrid exchange and Lee–Yang–Parr correlation functional (B3LYP). A 6-31G* basis set was used for all atoms. All geometry optimizations were performed in C1 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. 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-trifluoromethyl phenyl substituent at the 15-position was synthesized from DDQ oxidation of 2b) since this band is attributable to transitions between states that involve the LUMO+1, changes in the excited-state population of the LUMO$^+$ should display charge transfer character and therefore be sensitive to the polarity of the surrounding environment. Comparison of the UV–vis absorption profiles obtained for 3H(Phl(CF$_3$)) in a variety of solvents clearly shows that the phlorin displays solvatochroism (Figure 2a). Since the major transitions at $\sim$440 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 $\varepsilon = 2.3$ to 435 nm in acetonitrile ($\varepsilon = 36.6$). The low energy transitions at $\sim$665 nm show little variation as a function of solvent polarity (Figure 2b) since this band is attributable to transitions between states involving the HOMO and LUMO of 3H(Phl(CF$_3$)), and these frontier orbitals are not appreciably polarized.

Additional photophysical measurements recorded for 3H(Phl(CF$_3$)) revealed that this phlorin is weakly emissive with a fluorescence quantum yield of $\Phi_f = 5.70 \times 10^{-4}$ and associated excited-state lifetime of $\tau_f = 45$ ps in deaerated CH$_2$Cl$_2$. Both these values are in line with those observed for other electron deficient phlorin derivatives. Many polypyrrole platforms display a pronounced supramolecular chemistry via formation of hydrogen bonds between the pyrrole N–H moieties and fluoride. Titration of CH$_2$Cl$_2$ solutions of 3H(Phl(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(PhlCF₃) 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(PhlCF₃) in solvents of varying polarity. (b) Extent to which solvent polarity perturbs λₘₐₓ of the soret and Q-bands for 3H(PhlCF₃). (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, Job analysis showed that 3H(PhlCF3) is capable of binding up to two equivalents of F− to form 3H(PhlCF3)-2F− (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 βf = 1.6 × 1013 M−2 in CH2Cl2.

Binding of F− to 3H(PhlCF3) is very strong and persists in polar aprotic solvents. Titration of 3H(PhlCF3) in MeCN with TBAF leads to similar spectral changes in the visible and near-IR regions to those observed in CH2Cl2 (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 βf = 6.4 × 105 M−2 in this more polar solvent.

The observation that fluoride binding to 3H(PhlCF3) 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 CH2Cl2. We note that based on similar UV−vis titration experiments, 3H(PhlCF3) 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 3H(PhlCF3), 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,54,55 we set out to determine if a similar supramolecular chemistry exists for 3H(PhlCF3).

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

A solution of 3H(PhlCF3) 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 3H(PhlCF3) showed that the phlorin only binds one equivalent of acetate to form 3H(PhlCF3)-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 Kf = 440 for 3H(PhlCF3)-OAc−. These experiments represent the first demonstration that carboxylates can hydrogen-bond to the phlorin architecture. Moreover, the observation that 3H(PhlCF3)-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 3H(PhlCF3)-OAc− in MeCN is similar to that observed for formation of amidinium-carboxylate hydrogen bonding networks.61−63 Despite the appreciable formation constant for 3H(PhlCF3)-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 3H(PhlCF3)-OAc− disrupts these hydrogen-bonded assemblies, as evidenced by reversion of the UV−vis profile to that of uncomplexed 3H(PhlCF3) (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 pKf in MeCN that is very close in value to its smaller homologue (pKf of OAc− = 22.3; pKf of 3 = 23.0).54 Analysis of the binding data obtained upon titration of 3H(PhlCF3) with 3 reveals that the hydrogen-bonded assembly 3H(PhlCF3)-3 forms with a formation constant of Kf = 435. This titration experiment not only confirms that larger anions can bind to 3H(PhlCF3) 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 (pKf values for HF, HCl, and HBr in aprotic polar solvents are ∼15, 1.8, and 0.9, respectively).

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 3H(PhlCF3). 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 3H(PhlCF3) showed that each of the carboxylates form 1:1 adducts with the phlorin macrocycle. Table 1 summarizes the formation constants (Kf) for the corresponding 1:1 hydrogen-bonded 3H(PhlCF3) assemblies in MeCN, along with the corresponding pKf values for each of the carboxylates studied.54 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 3H(PhlCF3) in MeCN. For instance, the
addition of up to 3500 equiv of tetrabutylammonium 3,5-dinitrobenzoate (pKₐ = 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 3H(PhlCF₃) 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 3H(PhlCF₃) 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 3H(PhlCF₃) 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 Eₒₓ(1) = 0.42 V, Eₒₓ(2) = 0.67 V, and Eₒₓ(3) = 0.79 V versus Ag/AgCl. These values are in line with those observed for other electron deficient phlorins.⁶⁶ Just as hydrogen-bonding to the N–H groups of 3H(PhlCF₃) perturbs the phlorin spectral properties, the addition of either F⁻ or OAc⁻ to an MeCN solution of 3H(PhlCF₃) dramatically alters the phlorin redox properties. Formation of the F⁻ and OAc⁻ bound adducts (3H(PhlCF₃)-F⁻ and 3H(PhlCF₃)-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 is mirrored by the bathochromic shift observed for in the UV–vis absorbance spectrum upon binding of anions to 3H(PhlCF₃) (vide supra). In contrast to the electrochemical response observed upon binding of F⁻ to phlorins in CH₂Cl₂,₃₆ association of F⁻ or OAc⁻ with 3H(PhlCF₃) in MeCN causes the first and second oxidation waves to coalesce into a two electron wave (Eₒₓ = −0.14 and −0.13 V for 3H(PhlCF₃)-2F⁻ and 3H(PhlCF₃)-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 3H(PhlCF₃) displays an intriguing supramolecular chemistry with sufficiently basic anions, as this phlorin can cooperatively hydrogen-bond to two equivalents of F⁻ to form 3H(PhlCF₃)-2F⁻. Binding of fluoride to the N–H residues of 3H(PhlCF₃) is manifest in significant perturbation to the phlorin’s electronic structure and drives significant changes to the phlorin’s photophysical and redox properties.

Although 3H(PhlCF₃) 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, $3H(\text{Phl}^{\text{CF}_3})\cdot OAc^{-}$ 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 $3H(\text{Phl}^{\text{CF}_3})\cdot OAc^{-}$ 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 $3H(\text{Phl}^{\text{CF}_3})$ 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 $pK_a$ 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 $3H(\text{Phl}^{\text{CF}_3})$ to an appreciable extent in MeCN.

Furthermore, small anion guests such as nitrate 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 $3H(\text{Phl}^{\text{CF}_3})$ 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 $pK_a$ 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.

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