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Structural, spectroscopic and anion binding properties of 5,10-porphodimethenes, an unusual class of calixphyrins

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Complete spectroscopic, structural and anion binding properties are reported for a special class of calixphyrins, namely 5,10-disubstituted porphodimethenes (PDMs). The crystal structure clearly shows that PDMs exhibit nonplanar (distorted) structures with both sp^2 - and sp^3 -hybridized *meso* carbon centres. We were able to obtain and characterize the diacid form $[H_4(PDM)][X]_2$ upon addition of several acids to PDMs, where X denotes anions of different acids: HCl; HBr; MeSO₃H; CF₃CO₂H and HClO₄. We found that the PDM dications generated were more conjugated and thus more stable than their corresponding porphyrins. Their potential to coordinate anions was clearly shown using ¹H NMR spectroscopy. In addition, we found that when HClO₄ was used to protonate PDMs the conversion

occurs through an intermediate species, which has been assigned to the elusive monoacid derivative on the basis of UV-vis and ^1H NMR experiments.

KEYWORDS. Hydroporphyrin, nonplanarity, protonation, calixphyrins, receptors, tetrapyrrole monocation.

Introduction

Tetrapyrroles are a large class of compounds which comprise the fully conjugated porphyrins and the unconjugated calixpyrroles. Porphyrins are widespread in nature and increasingly used in medicine. They play an important role in photosynthesis¹ and have been proven as suitable photosensitizers in photodynamic therapy (PDT).² Calixpyrroles have been established as excellent anionic and neutral receptor systems.³ Anions are essential to life as many biological processes depend on their recognition, transport or transformation.⁴ They function in the majority of enzyme-substrate and enzyme-cofactor complexes as well as in the interaction between proteins and RNA or DNA.^{4,5} Conversely, anions have detrimental effects on the environment. Anionic pollutants such as phosphate and nitrate are the cause of eutrophication of lakes and inland waterways.⁶ There is a discernible demand for the production of selective anion receptors and sensors. Calix[4]pyrroles have been identified as neutral, non-aromatic polypyrrolic macrocycles that selectively bind anions.⁷ Likewise, sapphyrins, pentapyrrolic aromatic macrocycles, have been proven as excellent receptor systems when diprotonated.⁸

Calixpyrroles constitute four pyrrole units linked via sp^3 -hybridized *meso* carbon centres,⁹ as opposed to the sp^2 centres present in porphyrins.¹⁰ Porphodimethenes (PDMs)¹¹ belong to an intermediate class of compounds called calixphyrins (a hybrid of calixpyrroles and porphyrins) (Fig. 1).¹² They possess both sp^2 - and sp^3 -hybridized *meso* carbon centres. PDMs have the potential to possess both the binding properties of calixpyrroles along with the biological affinity of (hydro)porphyrins. Due to their appearance in the porphyrin biosynthetic pathway, 5,15-disubstituted PDMs have been thoroughly researched.¹³ The isomeric class, 5,10-disubstituted PDMs, however, has not received the same attention since it was first isolated in 1996 by Callot et al.^{14,15}

Previously our group reported on a more efficient synthesis of these tetrapyrroles,¹⁶ but until now, there have been no investigations into the coordination and ligand binding properties of these compounds, how they compare to porphyrins and their value as receptors. Thus, we have carried out in-depth research into 5,10-PDMs in order to more fully understand the properties and functionalities of this intriguing class of receptors.

Due to the presence of sp^3 -hybridized centres the macrocycles must adopt nonplanar conformations.^{11,15} The photophysical properties of nonplanar porphyrins differ significantly from those of their planar analogues (bathochromic shifts, larger Stokes shifts etc).^{17, 18} Generally nonplanarity is achieved in porphyrins by the introduction of complex substitution patterns on the porphyrin periphery, where steric bulk forces the macrocycle to distort. However it can also be achieved by the addition of two hydrogen atoms into the porphyrin core to produce the porphyrin dication. There is a vast conformational difference between the diprotonated porphyrin and that of the analogous free base macrocycle.¹⁹ The dication of 5,10,15,20-tetraphenylporphyrin, H_4TPP^{2+} , displays a similar saddle-type distortion to that of dodecasubstituted free base porphyrins such as 2,3,5,7,8,10,12,13,15,17,18,20-dodecaphenyl-porphyrin, H_2DPP .²⁰ There is a large catalogue of research papers dedicated to the chemistry, properties and applications of these molecules.^{21,22} Due to the significance of protons in essential biological processes and the effect of protonation on the porphyrin chemical and biological functions, a number of research groups have studied the porphyrin protonation process in the past decades. In *meso* arylporphyrins, the dication is formed in one step, without the isolation of an intermediate monocation. The differences in physical and chemical properties between the free base and the diprotonated species have been observed by using different acids such as trifluoroacetic acid, glacial acetic acid and perchloric acid.²¹⁻²⁵ To date, only limited research has been carried out on the effect of protonation and the properties of calixphyrin chemistry. This was an ideal starting point to investigate more closely the properties of PDM diacids and how they differ from their PDM and porphyrin analogues.

Experimental Methods

Porphyrins were synthesized by the standard Lindsey condensation method.²⁶ PDM **1** was synthesized by our previously reported method¹⁶ using 5,10,15,20-tetraphenylporphyrin as starting material and reacting this with phenyl lithium. All commercial chemicals and organolithium reagents were supplied by Aldrich and used without further purification. **Procedure for the synthesis of 2:** 5,10,15,20-Tetrakis(4-methoxyphenyl)porphyrin [H_2T -(4-MeOP)P] (100 mg, 0.14 mmol) was dissolved in 20 mL

THF. PhLi (0.75 mL, 1.36 mmol) was added at 0°C. The reaction mixture was heated 60 °C (TLC control) and quenched with saturated NH₄Cl (1 mL). The mixture was filtered through alumina (eluent: n-hexane) and the solvents were removed under reduced pressure. Purification was achieved by column chromatography on silica gel with n-hexane/ethyl acetate (4:1 v/v) to give the desired product (42.6 mg, 36.6 %); mp = 215°C R_f = 0.42 (SiO₂, nhexane/ ethyl acetate 3:1, v/v); ¹H NMR (600.13 MHz, CDCl₃) δ = 3.81 (s, 6 H, 5-OCH₃), 3.89 (s, 6 H, 20-OCH₃), 5.47 (d, 2 H, J = 2.3 Hz, β⁷-H), 6.09 (s, 2 H, β¹⁸-H), 6.16 (d, 2 H, J = 4.4 Hz, β³-H), 6.65 (d, 2 H, J = 4.6 Hz, β²-H), 6.77 (m, 4 H, 5^{mPh}-H), 6.94, (d, 4 H, J = 8.6 Hz, 20^{mPh}-H), 6.96 (m, 4 H, 5^{oPh}-H), 7.07 (m, 4 H, 5^{mPh}-H), 7.24 (m, 6 H, 5^{oPh}-H), 7.35 (d, 4 H, J = 8.4 Hz, 20^{oPh}-H), 10.58 (m, 1H, N²²-H), 12.58 (s, 1H, N²⁴-H), ¹³C NMR (100.6 MHz, CDCl₃) δ = 54.7 (CH₃), 54.9 (CH₃), 109.7 (β-H), 111.5 (Ar-C), 113.6 (Ar-C), 115.3 (Ar-C), 115.8 (Ar-C), 121.9 (β-H), 128.0 (Ar-C), 129.0 (β-H), (Ar-C), 129.0 (Ar-C), 134.7 (β-H) ppm; λ_{max} (log ε) = 324 (4.30), 380 (4.50), 451 (4.26), 566 (4.29) nm; HRMS (ES+) [C₆₀H₄₉N₄O₄+H] calcd. 889.3754, found 889.3758.

Crystal structure determination of 1: Growth and handling of crystals followed the concept developed by Hope.²⁷ Intensity data were collected at 108 K with a Saturn724 system complete with 3-circle goniometer and CCD detector utilizing Mo-K_α radiation (λ = 0.71073 Å). The intensities were corrected for Lorentz, polarization and extinction effects. The structure was solved with Direct Methods using the SHELXTL PLUS program system²⁸ and refined against |F²| with the program XL from SHELX-97 using all data.²⁹ Nonhydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were generally placed into geometrically calculated positions and refined using a riding model. The N-H hydrogen atoms were located in difference maps and refined using the standard riding model. Some of the phenyl groups showed high thermal librational movement. Refinement with split positions did not improve the refinement model. **Crystal data for 1:** C₅₆H₄₀N₄, M = 768.92, monoclinic, space group C2/c, a = 31.892(10), b = 13.983(4), c = 18.640(6) Å, β = 102.900(5), V = 8103(4) Å³, Z = 8, T = 108K, μ (Mo-K_α) = 0.074 cm⁻¹, 32429 reflections measured, 7107 unique

reflections measured ($R_{int} = 0.0815$), 541 parameters, 5257 reflections with $I > 2.0\sigma(I)$, refinement against $|F^2|$, $R1(I > 2.0\sigma(I)) = 0.0781$, $wR2$ (all data) = 0.2358, $S = 1.095$, $\rho_{max} = 0.614$.

UV-vis titrations were performed with a Perkin Elmer, Lambda 1050 spectrophotometer. Solutions of H₂TPP, H₂T-(4-MeOP)P (5,10,15,20-tetra-(4-methoxyphenyl)porphyrin), 5,5',10,10', 15,20-hexaphenylporphodimethene **1** and 5,10,15,20-tetra-(4-methoxyphenyl)-5',10'-diphenylporphodimethene **2** were prepared in spectrophotometric grade dichloromethane (Sigma). As not all materials were soluble in dichloromethane, HCl, HBr and HClO₄ were dissolved in spectrophotometric grade methanol, while MeSO₃H and TFA were soluble in dichloromethane. In order to assure that the protonation constant in dichloromethane is not dramatically affected by small amounts of methanol, a test titration was carried out with TFA in methanol. No noticeable differences were evident in the resulting spectra when compared to the corresponding titration with TFA in dichloromethane. UV-vis titrations were carried out by mixing 1×10^{-6} M solutions of H₂TPP and H₂T-(4-MeOP)P, and 1×10^{-5} M solutions of **1** and **2** with the appropriate acid. Up to 20 equiv. of acid were added to each tetrapyrrole, with TFA up to 100 equiv. were added. NMR spectra were recorded on a Bruker DPX 400 (400 MHz for ¹H NMR) and/or Bruker AV 600 (600 MHz for ¹H NMR and 100.6 MHz for ¹³C NMR). NMR titrations were either carried out in deuterated chloroform or deuterated dichloromethane, HCl and HClO₄ were dissolved in deuterated methanol. To rule out effects from the use of methanol, [H₄TPP](Cl)₂ was compared to previous results reported in the literature whereby protonation was achieved with TFA and subsequent anion coordination was accomplished with TBA-Cl to observe binding.³⁰ The resonances were comparable. 1×10^{-3} M solutions were prepared for ¹H NMR titrations. ¹H NMR titrations were not carried out with H₂T-(4-MeOP)P due to its low solubility. Up to 10 equiv. of acid were added to each tetrapyrrole, with TFA up to 100 equiv. were added.

Results

Crystallography

In order to establish the conformation and structural properties of the 5,10-PDM we were able to grow crystals suitable for single crystal X-ray crystallographic analysis of the 5,5',10,10',15,20-

hexaphenylporphodimethene **1**. The structure clearly shows the two sp^3 centres at the 5- and 10-position (Fig. 2). As expected, the macrocycle is highly nonplanar with a Δ_{24} of 0.40 Å for the 24 macrocycle atoms. Δ_{24} is the average deviation of the 24 macrocycle atoms from their least squares plane.¹⁷ The displacement of the *meso* carbon atoms is highly unsymmetrical. Displacement for the C5, C10, and C20 atoms from the 24 macrocycle atom least-squares-plane are 1.23, 1.22, 0.59 and 0.58 Å, respectively. The related values for deviation from the 4N plane are 0.85, 1.0, 0.95 and 0.83 Å, respectively. The conformation can roughly be described as an unsymmetrical roof-type conformation (as found for 5,15-PDM) with significant contributions from other distortion modes.²⁰ The two N-H vectors are pointed towards each other in the central core of the macrocycle. Thus, they are still somewhat shielded in this free base PDM and similar to the general situation found in planar porphyrins and *saddle* distorted nonplanar porphyrins.

We were able to obtain crystals of the dication of **1**, $[H_2\mathbf{1}][ClO_4]_2$. The compound crystallized with four independent molecules in the unit cell and included several solvent molecules. Together with low high angle reflection this resulted in a structure of only marginal quality (not shown). Thus only an overall conformational analysis can be given here. As expected, the structure is clearly more distorted than the free base **1**, and the four independent molecules exhibited Δ_{24} values of 0.62 to 0.66 Å. The displacement of the meso carbon was unsymmetric. For example, for one molecule the C5, C10, C15, and C20 displacements from the least-squares plane of the 24 macrocycle atoms were 0.46, -0.08, 0.24 and -0.2 Å, respectively. In the other molecules these values varied between 0 and 0.42 Å while b-displacements reached up to 1.4–1.5 Å. Thus, the asymmetry in the macrocycle distortion of the free base is retained in the dication.

UV-vis analysis

The UV-vis spectrum of 5,10-PDMs comprises two absorption bands, one at ~350 nm and the other at ~550 nm¹⁴ (Fig. 3). In 5,10-PDMs, the tetrapyrrole ring is divided into a tripyrrane unit and an isolated pyrrole unit (see Fig. 1). The tripyrrane moiety is responsible for these two broad absorbances, with the absorption due to the isolated pyrrole unit being too weak to be measured.³¹ This is considerably

different from the absorption spectrum of a porphyrin, where there is an intense Soret band at ~420 nm accompanied by four less intense Q bands at longer wavelengths.³² The absorption spectrum of a PDM is much less intense than that of the free base porphyrin. This is attributed to the interrupted conjugation in the PDM (Fig. 3).³³ UV-vis investigations were carried out on compounds **1** and **2** with several acids to determine the effect of protonation on the PDM macrocycle, to observe any anion effects that might occur and to compare the spectra to the analogous porphyrin.

The Soret band in the porphyrin UV-vis spectrum of H₂TPP was displaced to longer wavelengths upon protonation and the four Q bands were replaced by one more intense band at 665 nm (Fig. 3). This spectral simplification of porphyrin dications was attributed to the higher symmetry of porphyrin dications compared to that of their free base forms.³⁴ The porphyrin dications formed with acid halides gave absorbances that were more red shifted than those formed from the oxygen donor anions. The Soret band of the dication was of lower intensity than that of the respective free base *meso*-arylporphyrin. The UV-vis spectra of PDM dications displayed an intense absorption band at ca. 414 nm (**1**) or at ca. 425 nm (**2**) and a less intense band at ca. 630 nm (Fig 3). In both PDMs the MeSO₃H dication was most blue shifted, followed by TFA, with the HBr dication most red shifted. Upon addition of 2 equiv. of HCl, HBr and HClO₄, complete protonation of both PDMs was observed. 4.5 and 2.5 equiv. of MeSO₃H were required to fully protonate PDMs **1** and **2** respectively, whereas 70 (**1**) and 5 (**2**) equiv. of TFA were needed (Fig. 4). This trend was in agreement with the pK_a values of the acids.³⁵ The titration of TFA with both H₂TPP and **1** required over 40 equiv. of acid to form the dication, whereas with H₂T-(4-MeOP)P and **2**, less than 10 equiv. of acid were required. We have attributed this to a higher basicity of the pyrroline N atoms in the phenyl derivatives.

The UV-vis absorption spectra of the dications of compound **2** displayed an additional absorption band which was not present in the hexaphenyl derivative **1** (Fig. 5). In the area of 460-520 nm there was one broad absorption band that so far, we have been unable to account for. As similar equivalents of acid were required to fully protonate both PDMs, it is likely that the methoxy groups on the periphery influence the behavior of the PDM in solution.

PDMs **1** and **2** are non-aromatic species, and as such, were not expected to display fluorescence properties. Fluorescence measurements were performed to confirm this and indeed, no emission was observed.

NMR analysis

In order to elucidate the protonation in more detail, NMR titrations were carried out with H₂TPP and PDMs **1** and **2**. The ¹H NMR data collected for H₂TPP and **1** are in agreement with previous literature data.^{16,36}

The loss in aromaticity of the PDMs had an effect on the chemical shifts of the β- and N-protons. In the fully conjugated porphyrin, H₂TPP, the β-protons on the periphery of the macrocycle were strongly deshielded by the diamagnetic ring current. They resonated at 8.87 ppm. The N-protons, in the core of the macrocycle were shielded by the ring current and resonated upfield at -2.72 ppm (Fig. 6). In **1** and **2**, there is no ring current effect. This resulted in an upfield shift of the β-protons to between 5.46 and 6.65 ppm and a downfield shift of the NH-protons to 10.52 and 12.59 ppm (Fig. 6). **1** and **2** are of lower symmetry than the starting porphyrins. Instead of one resonance each for the β- and N-protons there were four and two resonances, respectively. The aromatic protons in porphyrins resonate at 7.81 and 8.28 ppm. In the PDMs they appeared further upfield at 7.06 and 7.24 ppm. The two additional aromatic rings appeared as a multiplet at 7.42 ppm. ¹H NMR titrations were carried out on **1** and **2** to observe the effect of protonation on the PDM spectra, of anions and of any binding that occurs.

Upon protonation of H₂TPP with TFA, the β-proton resonance at 8.87 ppm shifted upfield to 8.62 ppm and the aromatic protons shifted downfield ($\Delta\delta = 0.37 \pm 0.01$ ppm for the ortho protons and $\Delta\delta = 0.24$ ppm for the meta and para protons). The N protons were more sensitive to acid than the peripheral protons. The NH resonance shifted downfield by $\Delta\delta = 3.2$ ppm. The upfield shift of the β-protons and the downfield shift of the N protons relate to a decrease in the aromatic ring current with protonation.³⁷ When the concentration of acid was increased beyond the minimum amount required for dication formation, all aromatic and β-signals shifted downfield and all signals continuously shifted with

increasing acid concentration. The NH resonance shifted upfield by $\Delta\delta = 0.98$ ppm with 10 equiv. and $\Delta\delta = 1.44$ ppm with 100 equiv. This continuous shift was in agreement with previous literature data where it was reported that the resonances shifted continuously to limiting values in TFA solvent.³⁸ A similar trend was seen for the other acids. In $[\text{H}_4\text{TPP}](\text{Cl})_2$ the N protons shifted downfield by $\Delta\delta = 3.39$ ppm. With the addition of up to 10 equiv. of acid, an upfield shift was observed ($\Delta\delta = 0.64$ ppm). In $[\text{H}_4\text{TPP}](\text{ClO}_4)_2$ an overall shift of $\Delta\delta = 3.59$ ppm was observed and in $[\text{H}_4\text{TPP}](\text{MeSO}_3)_2$, $\Delta\delta = 3.72$ ppm.

In the ^1H NMR of the PDM dications of **1** and **2**, different behavior was observed. In contrast to the conjugated porphyrin, the β -protons shifted downfield by ca. 0.4 ppm upon protonation and the proton at N-22 (Fig. 7) moved upfield. Similar to the N protons in the porphyrin, the proton at N-24 shifted to lower field (Fig. 8) which was attributed to the proton being located at the more conjugated part of the PDM. This behavior suggested that the aromatic ring current was increasing with diprotonation, more noticeably at the unconjugated component of the macrocycle.. In the PDM dications, the resonance at 6.09 ppm (β -18 proton) displayed the largest downfield shift (up to $\Delta\delta = 0.86$ ppm) and the resonance at 5.46 ppm (β -7 proton) generally shifted the least, (however this cannot be said for all acids). The resonances at 6.65 and 6.16 ppm, attributable to β -2 and β -3 protons respectively, displayed similar downfield shifts upon protonation ($\Delta\delta = 0.53 \pm 0.07$ ppm).

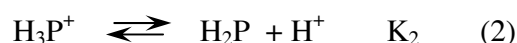
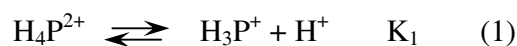
In each PDM dication, the proton at N-22 appeared as a split signal due to the presence of two stereoisomers (the same observation was made for the resonance due to the β -proton at C-7 where a singlet was expected) (Fig. 7). Using HClO_4 as the proton source, the β -protons shifted downfield by $\delta = 0.63$ ppm compared to 0.50 ± 0.05 ppm, 0.53 ± 0.01 ppm and 0.52 ± 0.01 ppm when the dication was formed with TFA, HCl and MeSO_3H respectively. Consequently, the proton at N-22 in $[\text{H}_4\text{PDM}](\text{ClO}_4)_2$ displayed the largest upfield shift from $\delta = 10.52$ to 8.94 ppm in $[\text{H}_4\mathbf{1}](\text{ClO}_4)_2$ and 10.56 to 8.65 ppm in $[\text{H}_4\mathbf{2}](\text{ClO}_4)_2$. When further aliquots of HClO_4 were added, a downfield shift was observed. Using MeSO_3H to form the PDM dication, the proton at N-22 shifted upfield and then shifted

further upfield upon addition of further amounts of acid ($\Delta\delta = 0.81 \pm 0.10$ ppm). Generally, the ^1H NMR resonances of the free base PDMs disappeared as those for the protonated species appeared. However, when the PDM dication was formed by protonation with TFA, the original resonances for the free base were only seen to shift. This also contrasted to the trend observed in the porphyrin. HCl displayed different behavior entirely, as the signal for the proton at N-22 appeared downfield at ca. 11.38 ppm (**1**) and 11.09 ppm (**2**) and then proceeded to shift upfield after further aliquots of acid were added ($\Delta\delta = 0.38 \pm 0.05$ ppm with 10 equiv.). This initial downfield shift, followed by an upfield shift was seen in the porphyrin dications.

Monocation intermediate

Upon protonation of PDMs **1** and **2** with HClO_4 , intermediate UV-vis and ^1H NMR spectra were observed which have been attributed to the presence of a monocation species. The observation of a monoprotonated porphyrin has rarely been reported before and proof of their existence has been the subject of considerable effort.^{19,25,39}

Free base porphyrins with two unprotonated N atoms are capable of exhibiting the following acid-base equilibria:



There have been many investigations into the above equilibria for various porphyrins and chlorins (2,3-dihydroporphyrins) using both potentiometric and spectrophotometric techniques.^{24,25,40} By more fully understanding the acid-base properties of tetrapyrroles, more information can be obtained on metal-macrocycle reactivity, π -electron delocalization, resonance energy N,N'-tautomerism, substitution pattern and stereochemistry.⁴¹

Both H_4P^{2+} and H_2P are very stable molecules, with the former possessing a four-fold axis of symmetry and the latter a two-fold. The difficulty in observing the monocation species of *meso*-arylporphyrins was attributed to loss of symmetry which decreased resonance stabilization and distorted the macrocycle. The monoprotonated derivative could therefore only exist over a very narrow pH range,

i.e. $K_1 \ll K_2$.^{19,21,25,30,42} In the UV-vis and ^1H NMR studies we carried out on the porphyrin, we found that the ring current decreased upon protonation. In the UV-vis studies this was shown by a less intense Soret band in the dication than in the free base. Whereas in the ^1H NMR titrations, a downfield shift of the N-protons and an upfield shift of the β -protons were consistent with a decrease in aromatic character and consequently, a decrease in stability. In contrast, in the PDM dications the “Soret” band was more intense and the chemical shifts in the NMR moved in the opposite directions, suggesting a more stable dication than free base form and conceivably, a more stable monocation.

Complex changes in the absorption profile of $\text{H}_2(\text{PDM}) \rightarrow [\text{H}_4\text{PDM}][\text{ClO}_4]_2$ pointed towards the occurrence of multiple equilibria in solution. This was attributed to the conversion of the free base species to its diacid form via the formation of a PDM monoprotonated at the core $[\text{H}_3\text{PDM}][\text{ClO}_4]$.

In PDM **1**, there was a shift in isosbestic points from 371 nm to 387 nm, from 466 nm to 493 nm and also a red shift from 606 nm in the monocation to 631 nm in the dication. A new maximum was observed at 732 nm. With the addition of 0.75 equiv. of acid to the PDM solution the absorbance at 732 nm reached a maximum, then weakened as further aliquots of acid were added (Fig. 9). These features pointed towards the presence of a chemically distinguishable monocation (Fig. 10). In **2** there was only a slight change in isosbestic points. Here the new absorption appeared at 719 nm after the addition of 0.75 equiv. of HClO_4 and disappeared after the addition of 1.50 equiv.

With less than the 2 equiv. per mole of H_2TPP required to convert the porphyrin completely to $\text{H}_4\text{TPP}^{2+}$, the ^1H NMR spectra contained a set of signals for each of the species at their expected chemical shift values. There were no signals at intermediate positions which could be attributed to a monoprotonated intermediate. In the ^1H NMR titration of PDM **1** and **2** with HClO_4 , intermediate spectra were observed (Fig. 11). The monocation was clearly detected by three sets of signals that were present between 0.25 and 1.75 equiv. In **2**, the C-20 methoxy resonance also showed an intermediate resonance. The free base resonated at 3.89 ppm, the monocation at 3.93 ppm and the dication at 3.97 ppm. Many resonances in the aromatic region overlapped so it was not possible to isolate a full set of signals for this intermediate species.

Conclusions

5,10-PDMs were found to exhibit highly nonplanar conformations. The effects of core protonation on 5,10-PDMs was investigated by UV-vis absorption and ^1H NMR spectroscopies. It was found that unlike their porphyrin analogues, PDM dications are more conjugated and therefore more stable than their free base counterparts. The PDM dications formed from acid halides gave absorbances that were more red shifted than those formed with the oxygen donor anions whereas the most dramatic changes in the ^1H NMR spectra occurred when the dication was formed with HClO_4 . We achieved a clear and distinct set of spectra which support the assignment of the monoprotonated species. We expect this may provide insight into the role of monoprotonated species in the coordination of metal ions into the hydroporphyrin macrocycle. In the ^1H NMR investigations, similar to porphyrins, PDMs were found to coordinate the acid anions. Thus, given the anion recognition features of sapphyrin dications, it is likely that the closely related PDMs could be used as receptors for small molecules and anions.

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Supporting Information Available. Corresponding UV-vis and ^1H NMR spectra to those shown within the article, together with HSQC and HMBC spectra of **2** are provided. This material is available free of charge via the Internet at <http://pubs.acs.org>. CCDC-XXXXXXX contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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Figure 1: sp^2 and sp^3 -carbon centres present in 5,15- (left) and 5,10-disubstituted porphodimethenes.

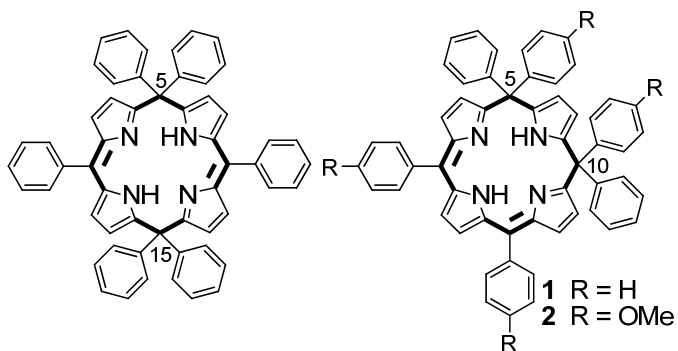


Figure 2: Top and side view of the molecular structure of PDM 1 in the crystal. Hydrogen atoms have been omitted for clarity and thermal ellipsoids are drawn for 40 % occupancy.

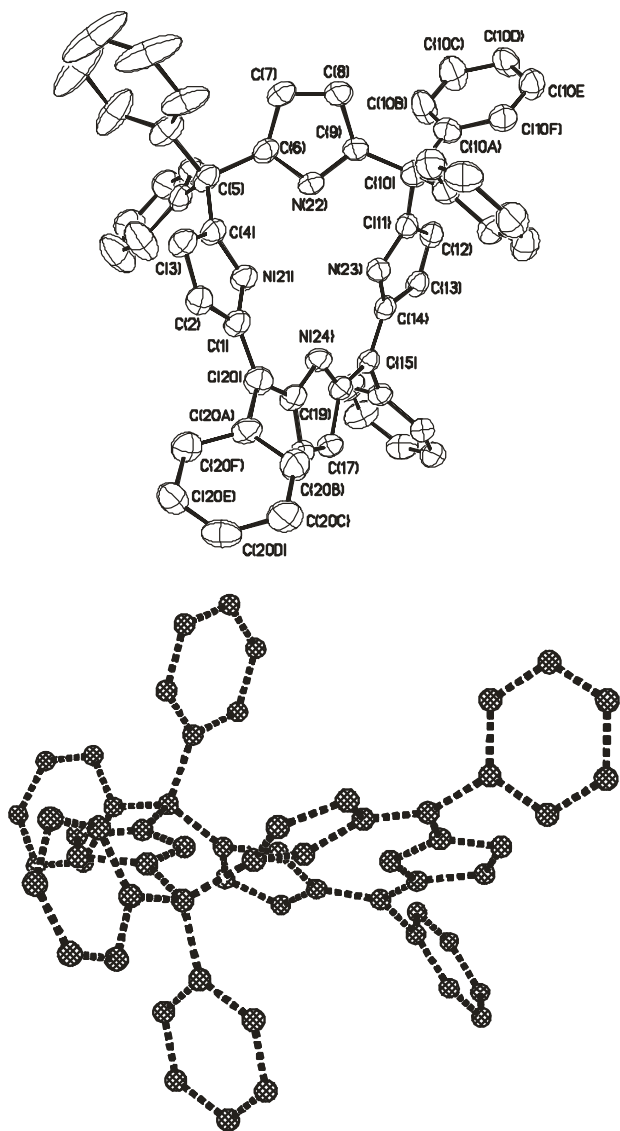


Figure 3: UV-vis Spectrum of PDM 1 (1×10^{-5} M) (black) versus that of the HClO_4 dication (grey) and H_2TPP (1×10^{-6} M) (black) versus that of the HClO_4 dication (grey) (inset) recorded in dichloromethane.

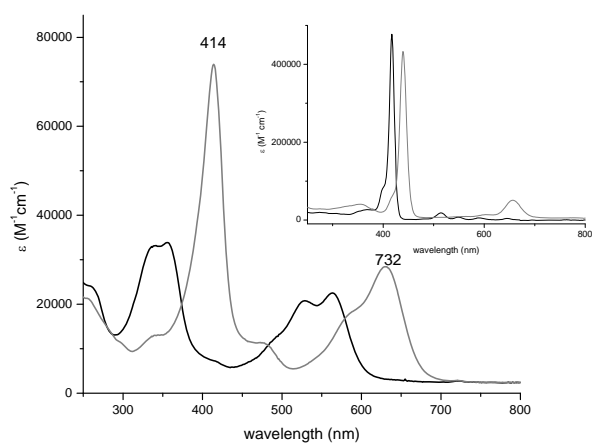


Figure 4: Relative absorption of PDM 2 (1×10^{-5} M) versus equivalents of acid recorded in dichloromethane.

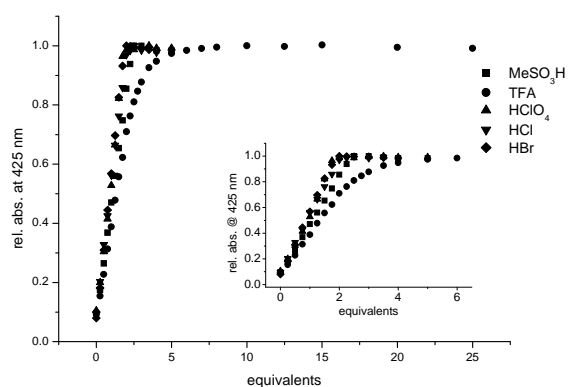


Figure 5: UV-vis titration of PDM 2 (1×10^{-5} M) with MeSO_3H recorded in dichloromethane.

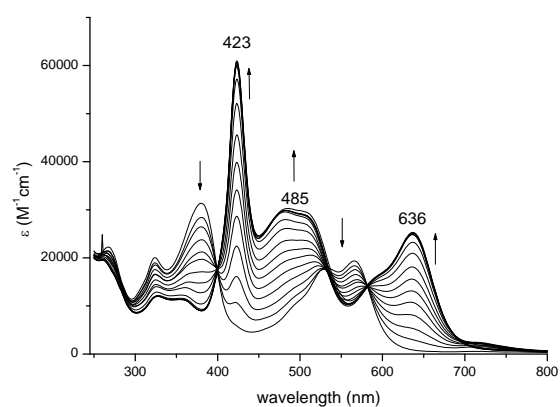


Figure 6: ^1H NMR spectra of H_2TPP (top) and PDM **1** (bottom) in CDCl_3 (1×10^{-3} M).

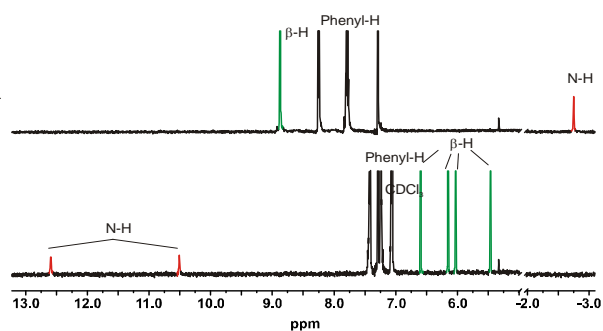


Figure 7: Possible stereoisomers of PDM **2** with IUPAC numbering.

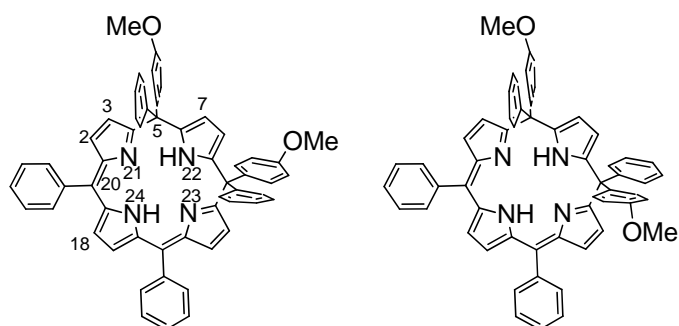


Figure 8: ^1H NMR spectral changes of the central protons $\text{N}^{24}/\text{N}^{21/23}$ (purple) and N^{22} (green) (left side), and β^7 - (green), β^{18} - (red), β^3 - (blue) and β^2 - (purple) (right side) observed upon the addition of MeSO_3H to PDM **2** (1×10^{-3} M) recorded in CDCl_3 .

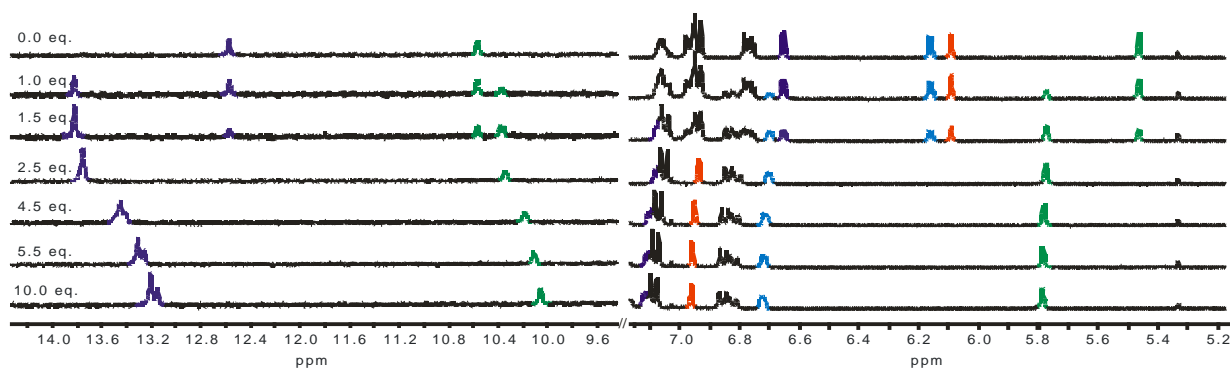


Figure 9: UV-vis titration of PDM **1** (1×10^{-5} M) with HClO_4 and relative absorption at 731 nm (inset) recorded in dichloromethane.

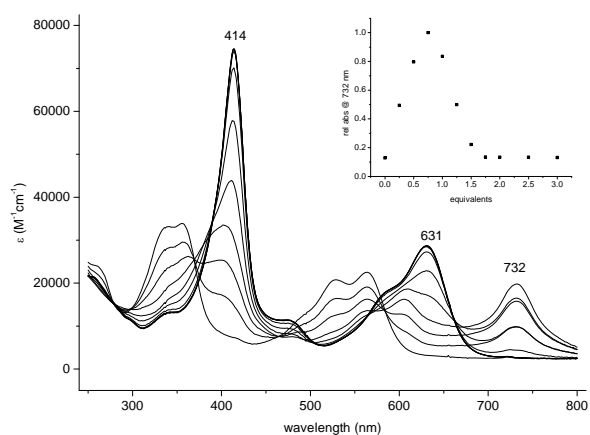


Figure 10: UV-vis spectrum of the monocation of PDM **1** (1×10^{-5}) derived from the spectral data in Fig. 9.

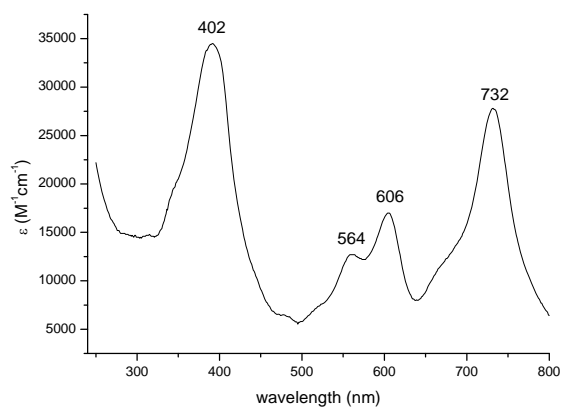
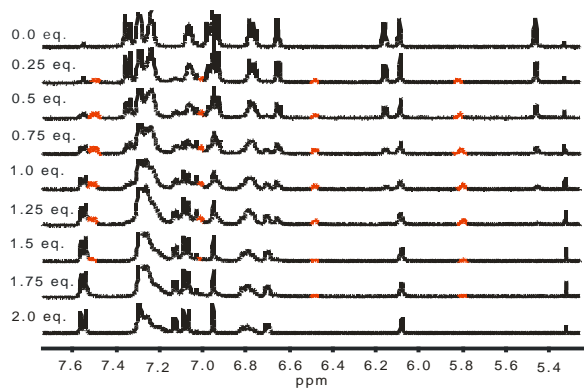


Figure 11: ^1H NMR titration of **2** (1×10^{-3} M) with HClO_4 (MeOD) in CD_2Cl_2 . Highlighted in red are the resonances due to a monocation species.



Structural, spectroscopic and anion binding properties of 5,10-porphodimethenes, an unusual class of calixphyrins

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Figure S1: UV-vis Spectrum of PDM **2** versus that of the HClO₄ dication and 5,10,15,20-tetrakis-(4-methoxyphenyl)porphyrin (H₂T-(4-MeOP)P) versus that of the HClO₄dication.

Figure S2: Relative absorption of PDM **1** (1 x 10⁻⁵M) versus equivalents of acid

Figure S3: Effect of the addition of MeSO₃H on the absorption spectrum of PDM **2**.

Figure S4: ¹H NMR spectra of H₂T-(4-MeOP)P and PDM **2** in CDCl₃.

Figure S5: HMBC and HSQC spectra of **2** highlighting the correlation between β⁷-H and N²²-H.

Figure S6: ¹H NMR spectral changes for the central protons observed upon addition of MeSO₃H to PDM **1**.

Figure S7: UV-vis titration of **2** with HClO₄ (MeOH) and relative absorption at 719 nm showing the absorption band due to the monocation.

Figure S8: ¹H NMR titration of **1** with HClO₄ (MeOD) in CD₂Cl₂. Highlighted are the resonances due to the monocation species.

Figure S1: UV-vis Spectrum of PDM **2** versus that of the HClO₄ dication and 5,10,15,20-tetrakis-(4-methoxyphenyl)porphyrin versus that of the HClO₄dication (inset).

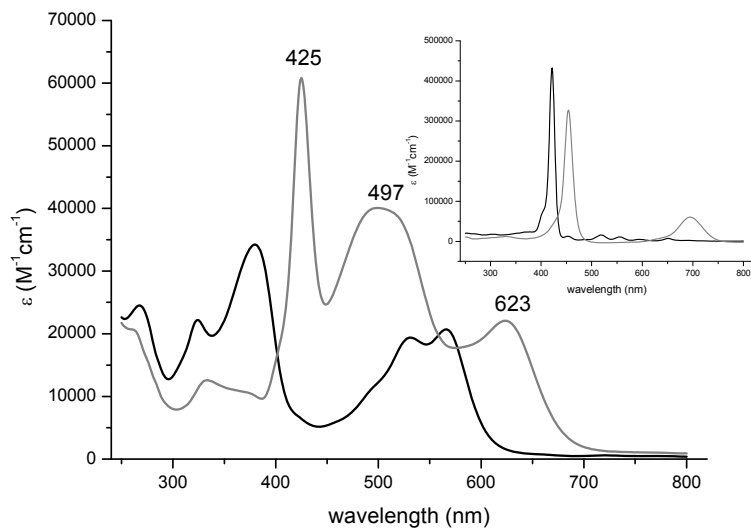


Figure S2: Relative absorption of PDM **1** (1×10^{-5} M) versus equivalents of acid recorded in dichloromethane

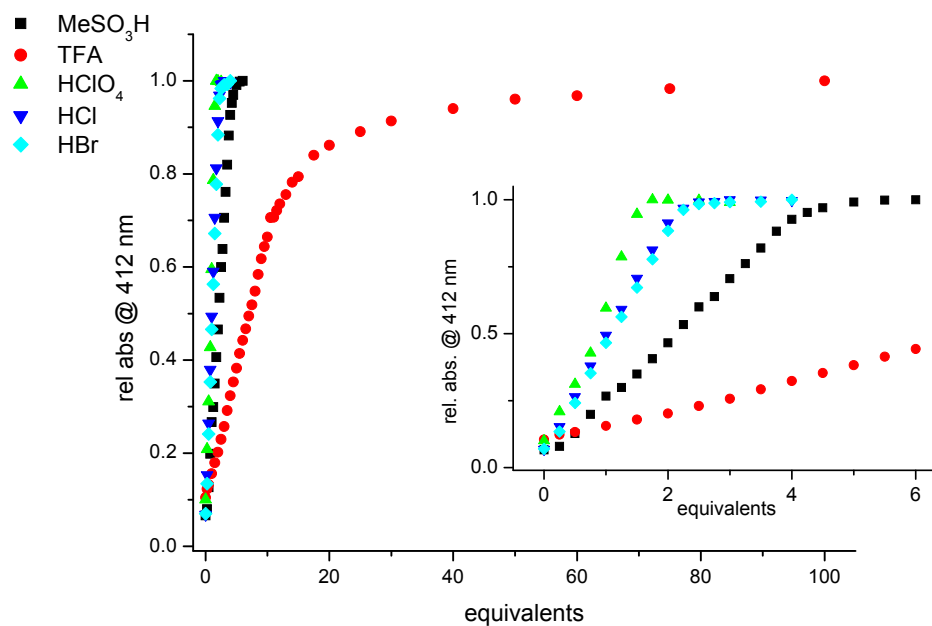


Figure S3: Effect of the addition of MeSO₃H on the absorption spectrum of PDM **1** in dichloromethane and plot of the absorption change of **2** at 409 nm vs. the equivalents of MeSO₃H (inset).

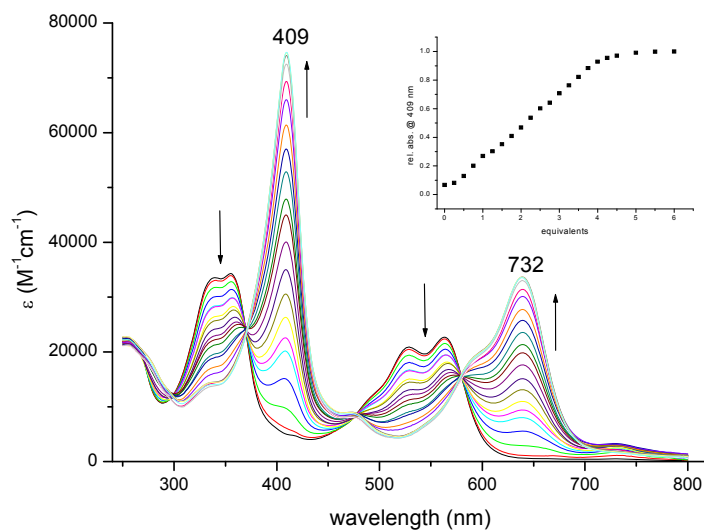


Figure S4: ¹H NMR spectra of H₂T-(4-MeOP)P (top) and PDM **2** (bottom) in CDCl₃.

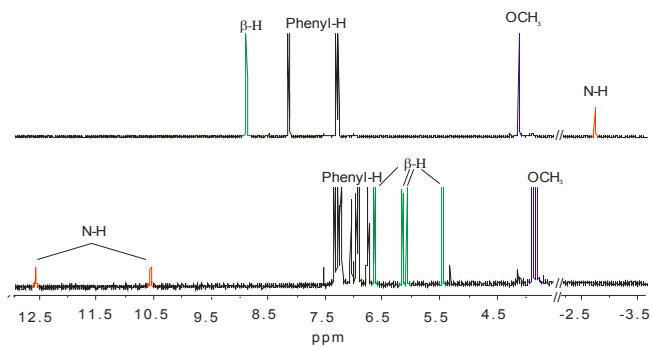


Figure S5: HMBC (blue) and HSQC (red) spectra of **2** in CDCl₃. The correlation between β^7 -H and N²² H is highlighted.

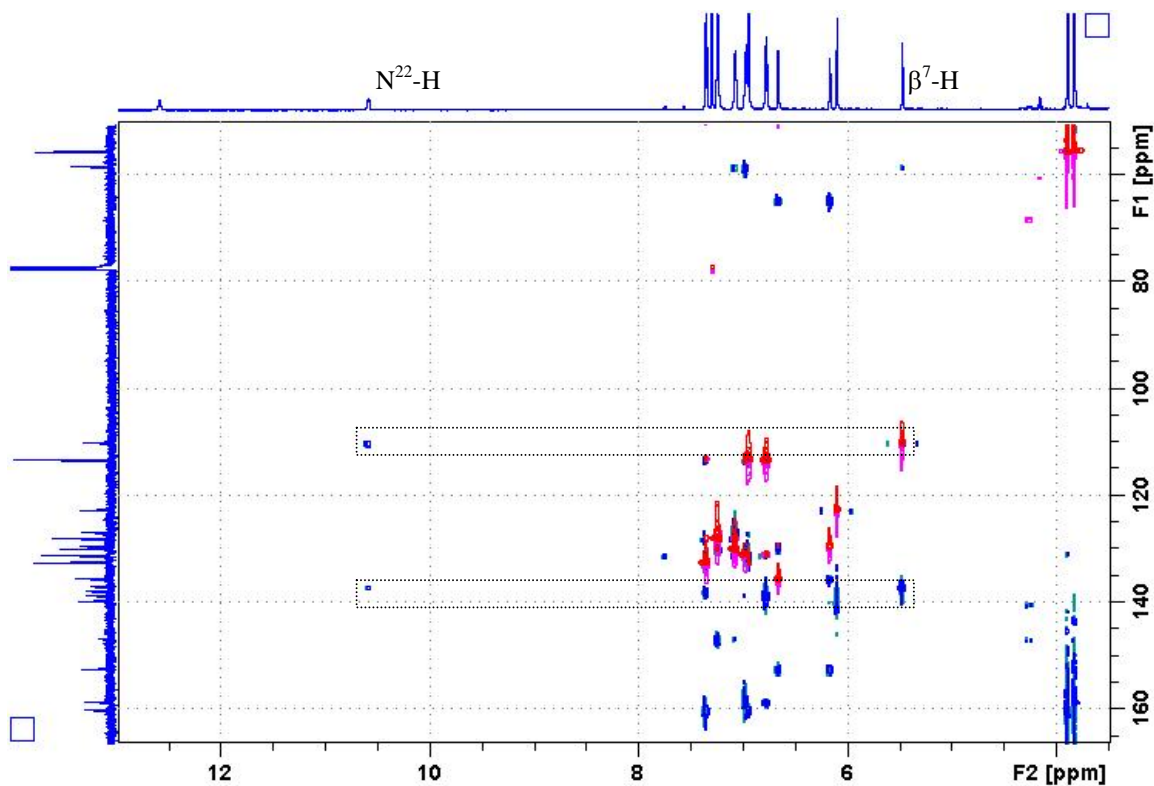


Figure S6: ¹H NMR spectral changes for the central protons N²⁴/N^{21/23} (purple) and N²² (green) (left side) and β^7 (green), β^{18} (red), β^3 (blue), and β^2 (purple) (right side) observed upon addition of MeSO₃H to PDM **1**.

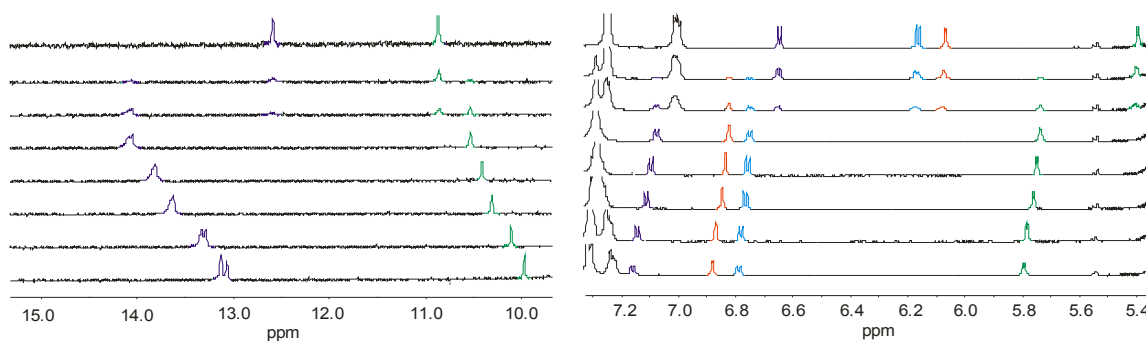


Figure S7 UV-vis titration of **2** with HClO₄ (MeOH) and relative absorption at 719 nm (inset) showing the absorption band due to the monocation.

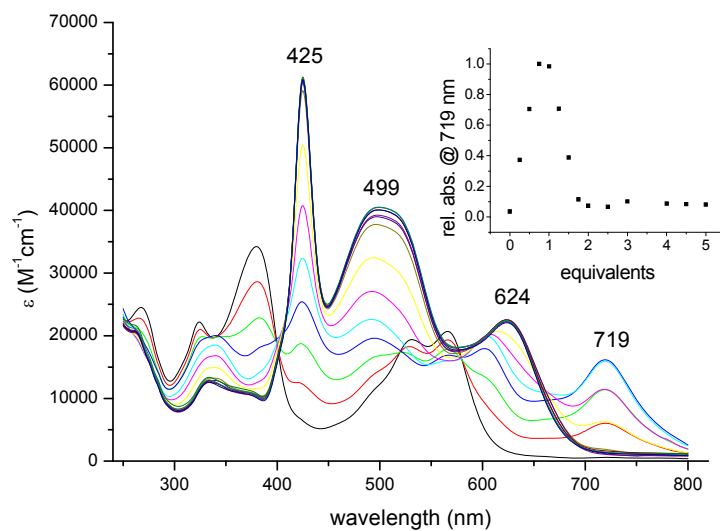


Figure S8: ¹H NMR titration of **1** with HClO₄ (MeOD) in CD₂Cl₂. Highlighted in red are the resonances due to the monocation species.

