

# Synthesis, Characterization, Protonation Reactions, and Electrochemistry of Substituted Open-Chain Pentapyrroles and Sapphyrins in Nonaqueous Media

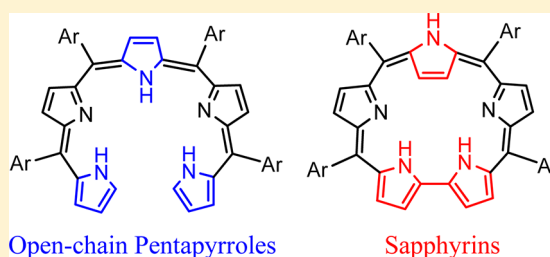
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## S Supporting Information

**ABSTRACT:** Open-chain pentapyrroles were isolated as side-products from the synthesis of triaryl-corroles and then converted to the corresponding sapphyrins by catalytic oxidation in acidic media. The investigated compounds were characterized by UV–vis and <sup>1</sup>H NMR spectroscopy, mass spectrometry, electrochemistry, and spectroelectrochemistry and are represented as (Ar)<sub>4</sub>PPyH<sub>3</sub> and (Ar)<sub>4</sub>SH<sub>3</sub>, where Ar is a F<sup>−</sup> or Cl<sup>−</sup> substituted phenyl group, PPy is a trianion of the open-chain pentapyrrole, and S is a trianion of the sapphyrin. Cyclic voltammetry and thin-layer UV–vis spectroelectrochemistry measurements were carried out in PhCN and CH<sub>2</sub>Cl<sub>2</sub> containing 0.1 M tetra-*n*-butylammonium perchlorate. The open-chain pentapyrroles undergo two reversible one-electron reductions and two reversible one-electron oxidations to generate [(Ar)PPyH<sub>3</sub>]<sup>−</sup>, [(Ar)PPyH<sub>3</sub>]<sup>2−</sup>, [(Ar)PPyH<sub>3</sub>]<sup>+</sup>, and [(Ar)PPyH<sub>3</sub>]<sup>2+</sup> which were spectroscopically characterized. The corresponding sapphyrins exhibit two or three reversible one-electron oxidations in PhCN, but the reductions of these compounds are irreversible because of coupled chemical reactions following electron transfer. Comparisons are made between redox potentials and spectral properties of the open-chain pentapyrroles, sapphyrins, and structurally related corroles. Protonation of the open-chain pentapyrroles and sapphyrins was also carried out in CH<sub>2</sub>Cl<sub>2</sub>, and equilibrium constants were calculated by monitoring the spectral changes during titrations with trifluoroacetic acid. The pentapyrroles undergo a simultaneous two-proton addition to generate [(Ar)<sub>4</sub>PPyH<sub>5</sub>]<sup>2+</sup> while the sapphyrins undergo two stepwise single proton additions to give [(Ar)<sub>4</sub>SH<sub>4</sub>]<sup>+</sup> and [(Ar)<sub>4</sub>SH<sub>5</sub>]<sup>2+</sup>, respectively.



## INTRODUCTION

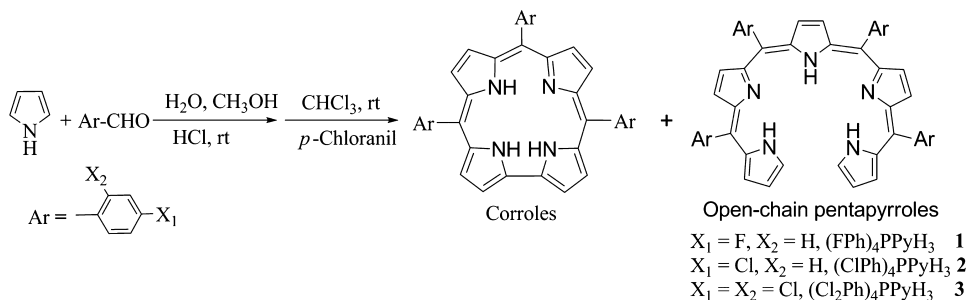
Sapphyrins have attracted a great deal of interest over the past decade<sup>1–11</sup> because of their similarity to porphyrins and their potential applications in many fields, including their use as functional materials, photosensitizers for photodynamic therapy (PDT) or magnetic resonance imaging (MRI) contrasting agents,<sup>1,7,12–16</sup> and macrocyclic receptors for the transport of neutral and anionic substrates.<sup>17–24</sup>

Sapphyrins are pentapyrrolic macrocycles containing one direct link and four bridging methane groups between five pyrrolic subunits.<sup>25</sup> These compounds have been described as  $\beta$ -pyrrole substituted macrocycles,<sup>26–29</sup> as N-fused or N-confused macrocycles<sup>30–33</sup> or as core-modified macrocycles with O, S, or Se heteroatoms.<sup>34–50</sup> A few N-5 *meso*-tetraaryl-substituted sapphyrins have also been reported<sup>51–54</sup> after isolation as a side-product from a Rothmund reaction in the synthesis of porphyrins<sup>51,52</sup> or from the one-step acid catalyzed self-coupling reaction of dipyrromethane.<sup>53</sup> An N-5 sapphyrin can also be synthesized by transformation of an open-chain pentapyrrole,<sup>54</sup> which is a side-product in the synthesis of corroles.<sup>53–56</sup>

Knowledge of the spectral and electrochemical properties of sapphyrins is important with respect to expanding the potential applications of these compounds in the field of biomedical and functional materials.<sup>1–8</sup> Although sapphyrins have been studied in great detail, there have been few reports on the electrochemical properties of N-5 *meso*-tetraaryl substituted sapphyrins. There is also very little known about the electrochemistry of open-chain pentapyrroles.

In the present paper, three substituted open-chain pentapyrroles were isolated as side-products from the synthesis of corroles after which the corresponding sapphyrins were synthesized by catalytic oxidation under acid conditions. Each pentapyrrole and sapphyrin was then characterized by UV–visible and <sup>1</sup>H NMR spectroscopy, mass spectrometry, electrochemistry, and spectroelectrochemistry. The investigated compounds are represented as (Ar)<sub>4</sub>PPyH<sub>3</sub> and (Ar)<sub>4</sub>SH<sub>3</sub>, where Ar is a F<sup>−</sup> or Cl<sup>−</sup> substituted phenyl group, PPy is a trianion of the open-chain pentapyrrole, and S is a trianion of the sapphyrin. Protonation of the open-chain pentapyrroles and

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Scheme 1. Synthetic Route for Obtaining Open-Chain Pentapyrroles<sup>a</sup>

<sup>a</sup>Ar is one of the substituted phenyl groups.

sapphyrins was monitored by UV–vis spectroscopy in CH<sub>2</sub>Cl<sub>2</sub> during a titration with trifluoroacetic acid (TFA), and the resulting spectroscopic data used to calculate equilibrium constants for these reactions.

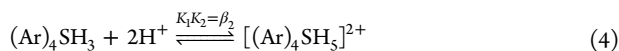
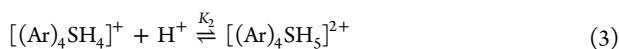
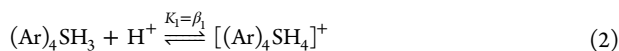
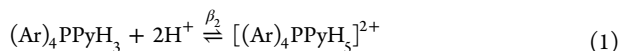
## EXPERIMENTAL SECTION

**Instrumentation.** Cyclic voltammetry was carried out at 298 K using an EG&G Princeton Applied Research (PAR) 173 potentiostat/galvanostat. A homemade three-electrode cell was used for cyclic voltammetric measurements and consisted of a platinum button or glassy carbon working electrode, a platinum counter electrode, and a homemade saturated calomel reference electrode (SCE). The SCE was separated from the bulk of the solution by a fritted glass bridge of low porosity which contained the solvent/supporting electrolyte mixture.

Thin-layer UV–visible spectroelectrochemical experiments were performed with a home-built thin-layer cell which has a light transparent platinum net working electrode. Potentials were applied and monitored with an EG&G PAR Model 173 potentiostat. Time-resolved UV–visible spectra were recorded with a Hewlett-Packard Model 8453 diode array spectrophotometer. High purity N<sub>2</sub> from Trigas was used to deoxygenate the solution and kept over the solution during each electrochemical and spectroelectrochemical experiment.

**Determination of Protonation Equilibrium Constants.** A series of CH<sub>2</sub>Cl<sub>2</sub> solutions containing trifluoroacetic acid (TFA) in different concentrations was prepared and used as the acid-titration reagent. Microliter quantities of TFA in CH<sub>2</sub>Cl<sub>2</sub> were added gradually to a 5.5 mL CH<sub>2</sub>Cl<sub>2</sub> solution of the open-chain pentapyrroles and sapphyrins in a homemade 1.0 cm cell, and the spectral changes monitored after each addition.

The prevailing protonation reaction is given by eq 1 for the open-chain pentapyrroles and eqs 2–4 for the sapphyrins.



Changes in UV–visible spectra during the titration with TFA were analyzed as a function of the concentration of added acid, using both the mole ratio method and the Hill equation<sup>57,58</sup> to calculate equilibrium constants for proton addition in the nonaqueous solvent, CH<sub>2</sub>Cl<sub>2</sub>.

**Chemicals.** Absolute dichloromethane (CH<sub>2</sub>Cl<sub>2</sub>) was purchased from Aldrich Co. and used as received for electrochemistry and spectroelectrochemistry. Benzonitrile (PhCN) was purchased from Aldrich Co. and distilled over phosphorus (P<sub>2</sub>O<sub>5</sub>) under vacuum prior to use. Tetra-*n*-butylammonium perchlorate (TBAP) was purchased from Sigma Chemical or Fluka Chemika Co., recrystallized from ethyl

alcohol, and dried under vacuum at 40 °C for at least one week prior to use.

**Synthesis of Open-Chain Pentapyrroles.** The examined open-chain pentapyrroles were obtained according to the synthetic route shown in Scheme 1. Substituted aldehyde (10 mmol) and pyrrole (30 mmol, 2.4 mL) were dissolved in a mixed solvent of CH<sub>3</sub>OH/H<sub>2</sub>O (30/30 mL) and after addition of 2.5 mL of HCl (36%), the solution was stirred at room temperature for 2.5 h. The reaction product was extracted with CHCl<sub>3</sub>, the organic layer washed twice with H<sub>2</sub>O, dried with Na<sub>2</sub>SO<sub>4</sub>, filtered, and then diluted to 150 mL with CHCl<sub>3</sub>. *p*-Chloranil (2.46 mg, 10 mmol) was added to the solution which was then refluxed for 4 h. The reaction mixture was passed over a silica column using CH<sub>2</sub>Cl<sub>2</sub> as eluent. The first collected red-color fraction contains the corroles, and the following fractions contain the pentapyrrole and other side-products. The latter fractions were combined and evaporated via vacuum distillation, and the pure product was obtained by chromatography of the concentrated mixture on Al<sub>2</sub>O<sub>3</sub> with CH<sub>2</sub>Cl<sub>2</sub>/hexane (5:1) as eluent.

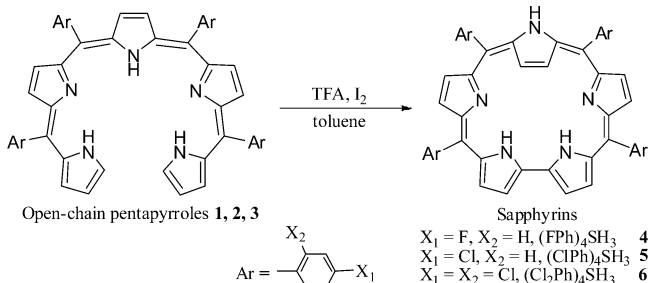
(FPh)<sub>4</sub>PPyH<sub>3</sub> 1. Yield 3%. UV–vis (PhCN): λ<sub>max</sub>, nm (ε × 10<sup>−4</sup> M<sup>−1</sup> cm<sup>−1</sup>) 382 (3.04), 446 (1.82), 501 (3.38), 825 (0.52), 903 (0.62). <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>COCD<sub>3</sub>): δ, ppm: 12.77 (br, s, 3H), 7.55–7.51 (m, 4H), 7.35–7.24 (m, 8H), 7.16 (t, J = 8.9 Hz, 4H), 6.71 (s, 2H), 6.62 (s, 2H), 6.58 (d, J = 4.6 Hz, 2H), 6.44 (d, J = 4.5 Hz, 2H), 6.06 (s, 4H). MS (MALDI-TOF): calcd. for C<sub>48</sub>H<sub>31</sub>F<sub>4</sub>N<sub>5</sub>, m/z 753.787, found [M+2H]<sup>2+</sup> 755.710.

(ClPh)<sub>4</sub>PPyH<sub>3</sub> 2. Yield 5%. UV–vis (PhCN): λ<sub>max</sub>, nm (ε × 10<sup>−4</sup> M<sup>−1</sup> cm<sup>−1</sup>) 384 (3.36), 450 (1.79), 505 (3.70), 830 (0.59), 907(0.73). <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>COCD<sub>3</sub>): δ, ppm: 12.77 (br, s, 3H), 7.56–7.51 (m, 8H), 7.45–7.41 (m, 4H), 7.33–7.28 (m, 4H), 6.79–6.77 (m, 2H), 6.63–6.57 (m, 4H), 6.49–6.46 (m, 2H), 6.11–6.04 (m, 4H). MS (MALDI-TOF): calcd. for C<sub>48</sub>H<sub>31</sub>Cl<sub>4</sub>N<sub>5</sub>, m/z 819.605, found [M+2H]<sup>2+</sup> 821.059.

(Cl<sub>2</sub>Ph)<sub>4</sub>PPyH<sub>3</sub> 3. Yield 5%. UV–vis (PhCN): λ<sub>max</sub>, nm (ε × 10<sup>−4</sup> M<sup>−1</sup> cm<sup>−1</sup>) 369 (3.45), 441 (1.45), 501 (4.00), 802 (0.62), 881(0.65). <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>COCD<sub>3</sub>): δ, ppm: 12.93 (br, s, 3H), 7.72–7.64 (m, 2H), 7.55–7.45 (m, 6H), 7.42–7.40 (m, 2H), 7.18–7.08 (m, 2H), 6.83–6.71 (m, 2H), 6.45–6.36 (m, 4H), 6.31–6.17 (m, 2H), 6.13–6.10 (m, 2H), 5.95 (br, 2H). MS (MALDI-TOF): calcd. for C<sub>48</sub>H<sub>27</sub>Cl<sub>8</sub>N<sub>5</sub>, m/z 957.385, found [M+2H]<sup>2+</sup> 959.722.

**Synthesis of Sapphyrins 4, 5, and 6.** Synthesis of the sapphyrins 4–6 was carried out as shown in Scheme 2. The pentapyrrole (20 mg) was dissolved in 20 mL of toluene and 0.2 mL of TFA and 9 mg of I<sub>2</sub> was added. The mixture was stirred for 7 h at 38 °C. The pure sapphyrin was obtained by chromatography, first on silica gel with CH<sub>3</sub>OH/CH<sub>2</sub>Cl<sub>2</sub> (98.5/1.5%) as eluent and then on an Al<sub>2</sub>O<sub>3</sub> column with CH<sub>2</sub>Cl<sub>2</sub> as eluent.

5,10,15,20-Tetrafluorophenylsapphyrin, (FPh)<sub>4</sub>SH<sub>3</sub> 4. Yield 19%. UV–vis (PhCN): λ<sub>max</sub>, nm (ε × 10<sup>−4</sup> M<sup>−1</sup> cm<sup>−1</sup>) 309 (1.03), 493 (6.57), 520 (4.29), 642 (0.41), 701 (0.76), 721(0.77), 797 (0.48). <sup>1</sup>H NMR (500 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ, ppm: 11.83 (br, 1H, NH), 10.10 (d, J = 4.6 Hz, 2H), 9.12 (d, J = 4.5 Hz, 2H), 9.05 (d, J = 4.4 Hz, 2H), 8.94 (t, J = 8.8 Hz, 2H), 8.35–8.27 (m, 6H), 7.56–7.53 (m, 4H), 7.46 (d, J = 8.3 Hz, 2H), 7.37 (m, 2H), 7.15–7.12 (m, 2H), −1.29 (m, 2H). MS

Scheme 2. Synthesis Route for Obtaining Sapphyrins<sup>a</sup>

<sup>a</sup>Ar is one of the substituted phenyl groups shown in Scheme 1.

(MALDI-TOF): calcd. for  $\text{C}_{48}\text{H}_{29}\text{F}_4\text{N}_5$ ,  $m/z$  751.771, found  $[\text{M} + 2\text{H}]^{2+}$  753.701.

5,10,15,20-Tetrachlorophenylsapphyrin,  $(\text{ClPh})_4\text{SH}_3$  **5**. Yield 25%. UV-vis (PhCN):  $\lambda_{\text{max}}$  nm ( $\epsilon \times 10^{-4} \text{ M}^{-1} \text{ cm}^{-1}$ ) 317(1.60), 498(9.37), 524 (6.33), 650 (0.59), 706 (1.19), 722 (1.22), 800 (0.68).

<sup>1</sup>H NMR (500 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta$ , 11.84 (s, 1H), 10.12 (d,  $J = 4.9$  Hz, 2H), 9.12 (d,  $J = 4.9$  Hz, 2H), 9.05 (d,  $J = 4.9$  Hz, 2H), 8.94 (d,  $J = 4.9$  Hz, 2H), 8.31–8.24 (m, 4H), 7.85–7.82 (m, 6H), 7.46–7.37 (m, 4H), 7.15–7.12 (m, 2H), –1.26 (s, 2H). MS (MALDI-TOF): calcd. for  $\text{C}_{48}\text{H}_{29}\text{Cl}_4\text{N}_5$ ,  $m/z$  817.589, found  $[\text{M} + \text{H}]^+$  818.859.

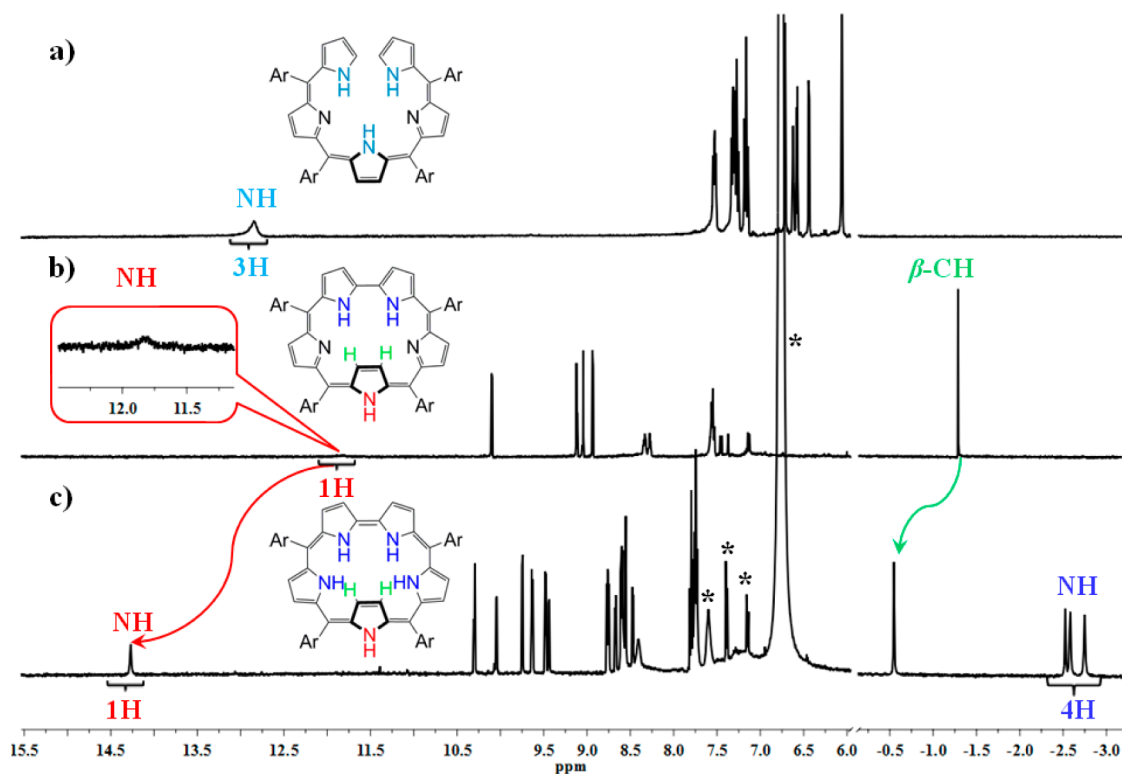
5,10,15,20-Tetra-2,4-dichlorophenylsapphyrin,  $(\text{Cl}_2\text{Ph})_4\text{SH}_3$  **6**. Yield 53%. UV-vis (PhCN):  $\lambda_{\text{max}}$  nm ( $\epsilon \times 10^{-4} \text{ M}^{-1} \text{ cm}^{-1}$ ) 316 (1.59), 494 (15.59), 517 (10.08), 637 (0.77), 695 (1.36), 711 (1.26), 787 (0.48). <sup>1</sup>H NMR (500 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta$  11.45–11.38 (m, 1H, NH), 10.15–10.08 (m, 2H), 9.27–9.24 (m, 1H), 9.02–8.97 (m, 2H), 8.86–8.71 (m, 3H), 8.30–8.07 (m, 3H), 7.99–7.90 (m, 2H), 7.78–7.71 (m, 2H), 7.63–7.61 (m, 0.5H), 7.48–7.37 (m, 2H), 7.15–6.95 (m, 2H), 6.88–6.86 (m, 0.5H), –1.30 to –1.49 (m, 2H). MS (MALDI-TOF): calcd. for  $\text{C}_{48}\text{H}_{25}\text{Cl}_8\text{N}_5$ ,  $m/z$  955.370, found  $[\text{M} + 2\text{H}]^{2+}$  957.011.

## RESULTS AND DISCUSSION

**Synthesis and Characterization.** The open-chain pentapyrroles were isolated as side-products in the synthesis of structurally related triarylcorroles (Scheme 1) and then converted to sapphyrins via cyclization in acidic media (Scheme 2) which gave the final product in yields ranging from 19 to 53%. Both series of compounds were characterized by UV-vis and <sup>1</sup>H NMR spectroscopy, mass spectrometry, and electrochemistry.

<sup>1</sup>H NMR spectra of  $(\text{FPh})_4\text{PPyH}_3$  **1**,  $(\text{FPh})_4\text{SH}_3$  **4**, and  $[(\text{FPh})_4\text{SH}_3]^{2+}$  are shown in Figure 1. The spectrum of  $(\text{FPh})_4\text{PPyH}_3$  is consistent with an open cycle molecular framework. The three NH protons appear as a broad peak located at 12.85 ppm while the phenyl and  $\beta$ -CH protons are located between 7.60 and 6.00 ppm. There are no resonances of the open-chain pentapyrrole **1** in the high field region of the spectrum (Figure 1a), but this is not the case for the related sapphyrin **4** (Figure 1b). Upon conversion of **1** to **4**, one of the three NH resonances is shifted upfield and appears as a broad and weak absorption located at 11.83 ppm. The other two NH resonances for **4** are too weak to be observed because of a rapid tautomeric equilibrium of the inner core NH.<sup>59</sup> The phenyl and  $\beta$ -CH protons both shift downfield upon conversion of **1** to **4**. The  $\beta$ -CH protons appear as four doublet signals at 10.10, 9.12, 9.05, and 8.94 ppm and a singlet signal at –1.29 ppm. These results indicate that two adjacent pyrrole rings of **4** are linked after oxidation, with one of the pyrrole rings being inverted to the outside of the molecule as shown by the structure in Figure 1b.

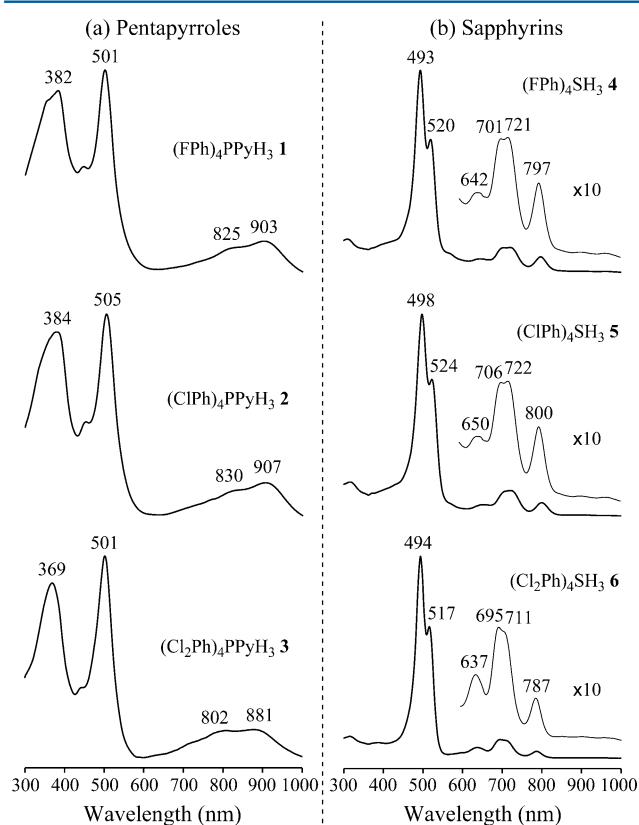
The NMR spectrum of protonated  $(\text{FPh})_4\text{SH}_3$  was generated by addition of trifluoroacetic acid to a  $\text{CD}_2\text{Cl}_2$  solution (1:20 molar ratio) to give  $[(\text{FPh})_4\text{SH}_3]^{2+}$ . The spectrum after



**Figure 1.** <sup>1</sup>H NMR spectra of (a)  $(\text{FPh})_4\text{PPyH}_3$  **1** in  $\text{CD}_3\text{COCD}_3$ , (b)  $(\text{FPh})_4\text{SH}_3$  **4**, and (c)  $[(\text{FPh})_4\text{SH}_3]^{2+}$  in  $\text{CD}_2\text{Cl}_2$  at 298 K. \*TFA and impurity peaks, Ar = FPh.

protonation is shown in Figure 1c and indicates that the molecule maintains its inverted structure. For instance, the outer NH proton together with the two inner  $\beta$ -CH protons are both shifted downfield and located at 14.27 ppm for the NH proton and  $-0.55$  ppm for the inner  $\beta$ -CH protons. The other NH protons are located at  $-2.52$  to  $-2.75$  ppm (see Figure 1c). The same phenomenon has been reported by Latos-Grażyński and co-workers.<sup>59</sup>

**UV–Visible Spectra.** UV–visible spectra of the open-chain pentapyrroles 1–3 and sapphyrins 4–6 were measured in  $\text{CH}_2\text{Cl}_2$  and PhCN containing 0.1 M TBAP. The absorption spectra in PhCN containing 0.1 M TBAP are illustrated in Figure 2, and the  $\lambda_{\text{max}}$  values of each compound are summarized



**Figure 2.** UV–visible spectra of neutral (a) pentapyrroles and (b) sapphyrins in PhCN containing 0.1 M TBAP.

in Tables 1 and 2. As seen in Figure 2a, the pentapyrrole 1 exhibits an intense split absorption band around 382 and 501 nm together with two moderate intensity absorption bands at 825 and 903 nm. Similar UV–visible spectra for the other two pentapyrroles are observed in PhCN and  $\text{CH}_2\text{Cl}_2$  (see Supporting Information, Figure S1a and Table 1).

UV–vis spectra of the related sapphyrins are shown in Figure 2b and differ significantly from the corresponding open-chain pentapyrroles under the same solution conditions. For example, sapphyrin 4 is characterized by a split Soret band at 493 and 520 nm and four Q bands at 642, 701, 721, and 797 nm in PhCN as compared to the pentapyrrole 1 which exhibits major bands at 382 and 501 nm and two broad overlapping bands at 825 and 903 nm. The spectrum of sapphyrins 5 and 6 are quite similar to that of 4 (see Figure 2b) and only a several nm difference can be observed in the Soret and Q-band positions of the three sapphyrins, indicating a weak effect of substituents on the UV–visible spectra under the given solution conditions. The UV–visible spectra of each sapphyrin are similar in  $\text{CH}_2\text{Cl}_2$  (Supporting Information, Figure S1b) as in PhCN (Figure 2b), consistent with identical structures existing in these two solvents.

The UV–visible spectra of the sapphyrins indicate compounds with a polypyrrolic aromatic macrocycle.<sup>50</sup> The Soret and Q bands of the sapphyrins are red-shifted from bands of the corroles and porphyrins containing identical substituents. For example,  $(\text{ClPh})_4\text{SH}_3$  4 in  $\text{CH}_2\text{Cl}_2$  (Supporting Information, Figure S1b) exhibits a split Soret band at 493, 518 nm and four Q bands at 649, 704, 724, and 800 nm as compared to the spectrum of *meso*-chlorophenyl substituted free-base corrole  $(\text{ClPh})_4\text{CorH}_3$  which has an unsplit Soret band at 417 nm and three Q bands at 578, 616, and 649 nm in the same solvent.<sup>56</sup>

It is well-known that the bi-, ter-, and quaterpyrroles can be protonated to give the corresponding cations and dications upon addition of acid to solutions of the compound,<sup>60–62</sup> and the currently investigated open-chain pentapyrroles can also be protonated as shown by eq 1. An example of the spectral changes which occur during titration of  $(\text{Cl}_2\text{Ph})_4\text{PPyH}_3$  3 with trifluoroacetic acid in  $\text{CH}_2\text{Cl}_2$  as solvent is shown in Figure 3a. The final spectrum of the protonated pentapyrrole is characterized by bands at 403, 514, and 876 nm (Figure 3a). The slope (2.0) from the Hill plot, shown as an inset in Figure 3a, indicates a single step, bis-protonation reaction to generate the dication,  $[(\text{Cl}_2\text{Ph})_4\text{PPyH}_5]^{2+}$ . The protonation constant was calculated as  $\log \beta_2 = 8.1$  for compound 3 in  $\text{CH}_2\text{Cl}_2$ , and similar values of  $\log \beta_2$  were calculated for the bis-protonated compounds 1 and 2 under the same solution conditions (Table 3). UV–vis spectra of the three bis-protonated open-chain pentapyrroles and the calculated  $\log \beta_2$  values are summarized in Table 3.

Sapphyrins can also be protonated in acidic solutions, leading to mono and bis-protonated species with different UV–visible spectra from that of the neutral compound.<sup>51,59</sup> An example of the spectral changes which occur for compound 4 during a titration with TFA in  $\text{CH}_2\text{Cl}_2$  is shown in Figure 3b. As seen from this figure, two sets of well-defined spectral changes are observed during the titration, indicating two stepwise

**Table 1.** UV–Visible Spectral Data of Open-Chain Pentapyrroles 1–3 in PhCN and  $\text{CH}_2\text{Cl}_2$  Containing 0.1 M TBAP

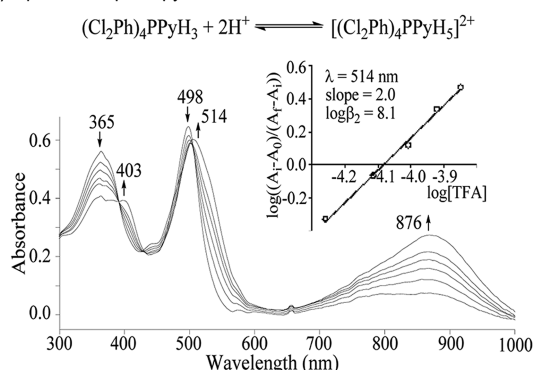
solvent	compound	$\lambda_{\text{max}}$ nm ( $\epsilon \times 10^{-4} \text{ M}^{-1} \text{ cm}^{-1}$ )			
PhCN	$(\text{FPh})_4\text{PPyH}_3$ 1	382 (3.04)	501 (3.38)	825 (0.52)	903 (0.62)
	$(\text{ClPh})_4\text{PPyH}_3$ 2	384 (3.36)	505 (3.70)	830 (0.59)	907 (0.73)
	$(\text{Cl}_2\text{Ph})_4\text{PPyH}_3$ 3	369 (3.45)	501 (4.00)	802 (0.62)	881 (0.65)
$\text{CH}_2\text{Cl}_2$	$(\text{FPh})_4\text{PPyH}_3$ 1	371 (3.28)	498 (3.61)	810 (0.57)	896 (0.71)
	$(\text{ClPh})_4\text{PPyH}_3$ 2	376 (3.75)	502 (4.15)	815 (0.68)	896 (0.81)
	$(\text{Cl}_2\text{Ph})_4\text{PPyH}_3$ 3	369 (3.90)	499 (4.47)	794 (0.61)	866 (0.63)



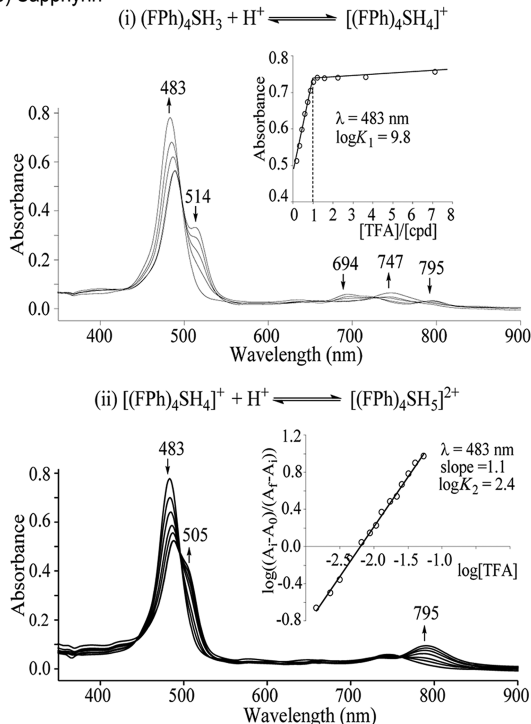
Table 2. UV-Visible Spectral Data of Sapphyrins 4–6 in PhCN and CH<sub>2</sub>Cl<sub>2</sub> Containing 0.1 M TBAP

solvent	compound	$\lambda_{\text{max}}$ nm ( $\epsilon \times 10^{-4} \text{ M}^{-1} \text{ cm}^{-1}$ )					
PhCN	(FPh) <sub>4</sub> SH <sub>3</sub> 4	493 (6.57)	520 (4.29)	642 (0.41)	701 (0.76)	721 (0.77)	797 (0.48)
	(ClPh) <sub>4</sub> SH <sub>3</sub> 5	498 (9.37)	524 (6.33)	650 (0.59)	706 (1.19)	722 (1.22)	800 (0.68)
	(Cl <sub>2</sub> Ph) <sub>4</sub> SH <sub>3</sub> 6	494 (15.59)	517 (10.08)	637 (0.77)	695 (1.36)	711 (1.26)	787 (0.48)
CH <sub>2</sub> Cl <sub>2</sub>	(FPh) <sub>4</sub> SH <sub>3</sub> 4	489 (9.55)	514 (5.71)	635 (0.48)	694 (0.94)	722 (0.78)	795 (0.51)
	(ClPh) <sub>4</sub> SH <sub>3</sub> 5	493 (9.28)	518 (5.86)	649 (0.47)	704 (0.97)	724 (0.83)	800 (0.50)
	(Cl <sub>2</sub> Ph) <sub>4</sub> SH <sub>3</sub> 6	488 (16.12)	511 (9.70)	629 (0.84)	687 (1.28)	714 (1.02)	787 (0.45)

## (a) Open-chain pentapyrrole



## (b) Sapphyrin



**Figure 3.** UV–visible spectral changes of (Cl<sub>2</sub>Ph)<sub>4</sub>PPyH<sub>3</sub> 3 and (FPh)<sub>4</sub>SH<sub>3</sub> 4 during a titration with TFA in CH<sub>2</sub>Cl<sub>2</sub> (insets are the molar ratio plot and Hill plot for determination of the number of protons and protonation equilibrium constants).

protonation reactions to give  $[(\text{FPh})_4\text{SH}_4]^+$  and  $[(\text{FPh})_4\text{SH}_5]^{2+}$ , respectively. The relevant reactions are given by eqs 2 and 3, and the calculated equilibrium constants of  $\log K_1 = 9.8$  and  $\log K_2 = 2.4$  are listed in Table 3 which also includes the UV–visible spectral data for  $[(\text{Ar})_4\text{SH}_4]^+$  and  $[(\text{Ar})_4\text{SH}_5]^{2+}$  in CH<sub>2</sub>Cl<sub>2</sub>.

## Electrochemistry of the Open-Chain Pentapyrroles.

Electrochemical properties of the open-chain pentapyrroles 1–3 were evaluated in CH<sub>2</sub>Cl<sub>2</sub> and PhCN containing 0.1 M TBAP as supporting electrolyte. Examples of cyclic voltammograms are shown in Figure 4 (CH<sub>2</sub>Cl<sub>2</sub>) and Supporting Information, Figure S2 (PhCN) while the reduction/oxidation potentials are summarized in Table 4.

Each open-chain pentapyrrole exhibits two reversible one-electron reductions and two reversible one-electron oxidations. The difference in half-wave potentials between the first and the second reduction is given in Table 4 as  $\Delta E_{1/2(1r-2r)}$  and ranges from 0.23 to 0.32 V. The potential difference between the first and second oxidation,  $\Delta E_{(2o-1o)}$ , ranges from 0.23 to 0.39 V and is also given in Table 4. Both separations are similar to  $\Delta E_{1/2}$  values often reported for ring-centered reductions and oxidations of free-base porphyrins.<sup>63</sup>

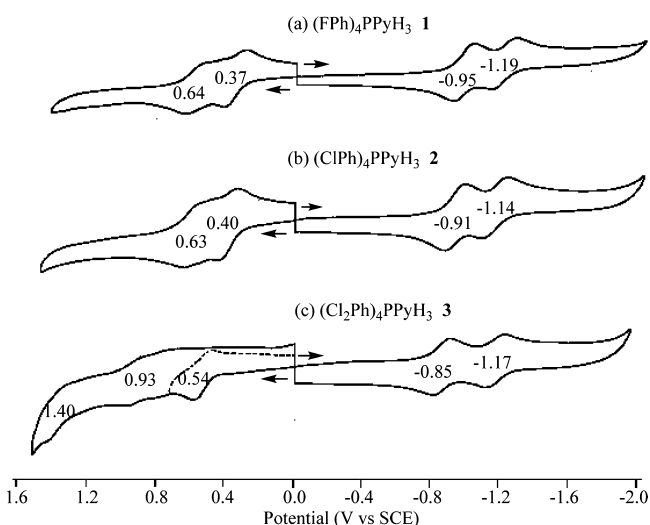
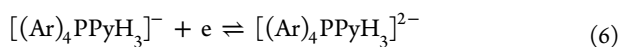
As expected, the measured  $E_{1/2}$  values for oxidation and reduction of 1–3 vary with the specific electron-withdrawing substituent at the four phenyl rings of the compound, and a linear relationship is observed between the  $E_{1/2}$  and the Hammett constants of the substituents<sup>64</sup> as shown in Figure 5. The slope of the correlation in the plots of Figure 5 are defined by the equation  $\Delta E_{1/2} = \sum \sigma \rho$ , where  $\sum \sigma$  represents the sum of the substituent constants and  $\rho$  is the reaction constant.<sup>64</sup> The values of  $\rho$  for the first reduction and first oxidation of the open-chain pentapyrroles were calculated as 117 and 68 mV, respectively and are similar to values of reaction constants obtained in the case of free-base porphyrins.<sup>63</sup> The absolute potential differences between the first reduction and first oxidation (the gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO)) ranged from 1.31 to 1.39 V in CH<sub>2</sub>Cl<sub>2</sub> (Table 4) with an average value of  $1.34 \pm 0.04$  V as shown in the figure. This HOMO–LUMO gap is much smaller than that of porphyrins which generally averages  $2.25 \pm 0.15$  V for the ring-centered reactions of free-base porphyrins.<sup>63</sup>

The UV–visible spectra of each pentapyrrole in CH<sub>2</sub>Cl<sub>2</sub> and PhCN were obtained after electroreduction or electrooxidation in a thin-layer cell. An example of the time-resolved spectral changes obtained during the first and second controlled-potential reductions of (Cl<sub>2</sub>Ph)<sub>4</sub>PPyH<sub>3</sub> 3 in CH<sub>2</sub>Cl<sub>2</sub> is shown in Figure 6a. Two well-defined sets of spectral changes are seen, corresponding to the stepwise formation of  $[(\text{Cl}_2\text{Ph})_4\text{PPyH}_3]^-$  and  $[(\text{Cl}_2\text{Ph})_4\text{PPyH}_3]^{2-}$  under the application of an applied reducing potential. Almost identical spectral changes were observed for the other open-chain pentapyrroles upon controlled potential reductions in the same solvent. The electrode reactions are described by eqs 5 and 6 where the stepwise reduction products are assigned as a  $\pi$ -anion radical and dianion, respectively.

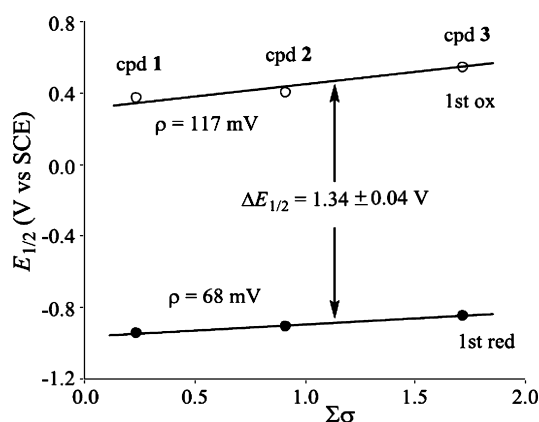


**Table 3.** UV-Visible Spectral Data ( $\lambda_{\text{max}}$ , nm) of Protonated Open-Chain Pentapyrroles 1–3 and Sapphyrins 4–6 in  $\text{CH}_2\text{Cl}_2$  with Added TFA and the Protonation Constants

cpd	final protonated form	$\lambda_{\text{max}}$ , nm			protonation constant <sup>a</sup>
1	$[(\text{FPh})_4\text{PPyH}_5]^{2+}$	400	524	915	$\log \beta_2 = 11.0$
2	$[(\text{ClPh})_4\text{PPyH}_5]^{2+}$	404	526	914	$\log \beta_2 = 9.1$
3	$[(\text{Cl}_2\text{Ph})_4\text{PPyH}_5]^{2+}$	403	514	876	$\log \beta_2 = 8.1$
4	$[(\text{FPh})_4\text{SH}_4]^+$	483	655	747	$\log K_1 = 9.8$
5	$[(\text{ClPh})_4\text{SH}_4]^+$	488	657	752	$\log K_1 = 9.2$
6	$[(\text{Cl}_2\text{Ph})_4\text{SH}_4]^+$	481	651	748	$\log K_1 = 7.5$
4	$[(\text{FPh})_4\text{SH}_5]^{2+}$	488	586	655	$\log K_2 = 2.4$
5	$[(\text{ClPh})_4\text{SH}_5]^{2+}$	492	596	659	$\log K_2 = 2.7$
6	$[(\text{Cl}_2\text{Ph})_4\text{SH}_5]^{2+}$	499	586	659	$\log K_2 = 1.3$

<sup>a</sup>See eq 1 for compounds 1–3 and eqs 2–4 for compounds 4–6.**Figure 4.** Cyclic voltammograms of open-chain pentapyrroles 1–3 in  $\text{CH}_2\text{Cl}_2$  containing 0.1 M TBAP.

The thin-layer spectral changes obtained during controlled-potential oxidation of  $(\text{Cl}_2\text{Ph})_4\text{PPyH}_3$  3 in  $\text{CH}_2\text{Cl}_2$  are illustrated in Figure 6b. The first oxidation at an applied potential of 0.70 V leads to a spectrum with bands at 406, 530, and 889 nm. This spectrum is very similar to the UV–visible spectrum of the bis-protonated form of compound 3,  $[(\text{Cl}_2\text{Ph})_4\text{PPyH}_5]^{2+}$ , which has bands at 403, 514, and 876 nm (Figure 3a). Similar UV–visible spectra are also seen after the one-electron oxidation of compounds 1 and 2, and these

**Figure 5.** Plots of half-wave potentials for the first reduction and first oxidation of compounds 1–3 in  $\text{CH}_2\text{Cl}_2$  containing 0.1 M TBAP vs the Hammett substituent constants ( $\Sigma\sigma$ ). Values of  $E_{1/2}$  and  $\Sigma\sigma$  are given in Table 4.

spectra also resemble spectra of the doubly protonated open-chain pentapyrroles,  $[(\text{FPh})_4\text{PPyH}_5]^{2+}$  and  $[(\text{ClPh})_4\text{PPyH}_5]^{2+}$ .

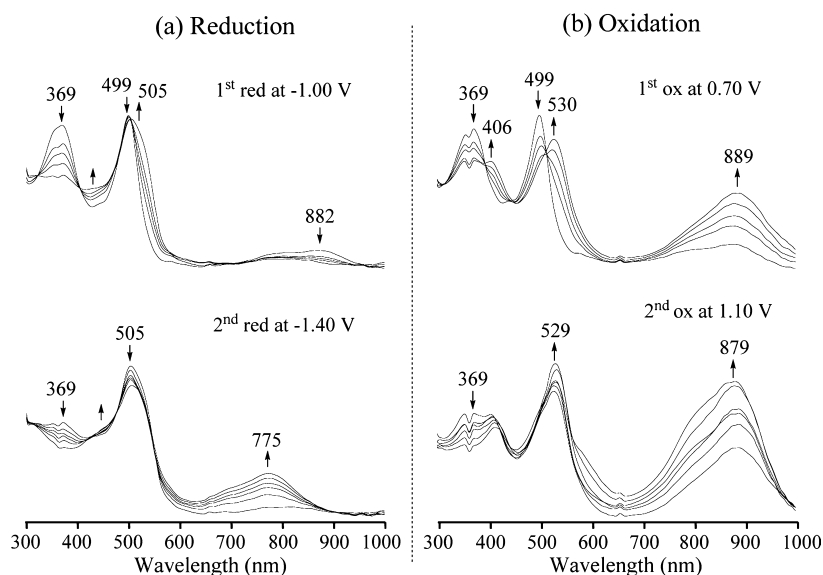
The fact that very similar UV–visible spectra are seen after controlled potential oxidation of 1–3 in  $\text{CH}_2\text{Cl}_2$  and after addition of TFA to the neutral compounds in  $\text{CH}_2\text{Cl}_2$  suggests that a protonation is occurring in both cases. Oxidation-induced protonation reactions have previously been reported for other open chain oligopyrrole systems<sup>61,62</sup> as well as for oxidized free-base corroles<sup>65,66</sup> and oxidized free-base porphyrins.<sup>67</sup>

Although the time-resolved spectra during the first oxidation of  $(\text{Cl}_2\text{Ph})_4\text{PPyH}_3$  3 at 0.70 V pass through two well-defined isosbestic points (at 395 and 515 nm), isosbestic behavior is not observed during the second oxidation at a controlled potential of 1.10 V. These spectral changes are shown in the

**Table 4.** Half-Wave Potentials (V vs SCE) of Substituted Pentapyrroles in  $\text{CH}_2\text{Cl}_2$  and PhCN, 0.1 M TBAP

solvent	compound	$4\sigma^a$	oxidation				reduction			HOMO–LUMO gap (V) <sup>e</sup>
			third	second	first	$\Delta E(2\text{o}-1\text{o})^c$	first	second	$\Delta E_{1/2}(1\text{r}-2\text{r})^d$	
$\text{CH}_2\text{Cl}_2$	$(\text{FPh})_4\text{PPyH}_3$ 1	0.24		0.64	0.37	0.27	−0.95	−1.19	0.24	1.32
	$(\text{ClPh})_4\text{PPyH}_3$ 2	0.92		0.63	0.40	0.23	−0.91	−1.14	0.23	1.31
	$(\text{Cl}_2\text{Ph})_4\text{PPyH}_3$ 3	1.72	1.40	0.93	0.54	0.39	−0.85	−1.17	0.32	1.39
PhCN	$(\text{FPh})_4\text{PPyH}_3$ 1	0.24		0.58 <sup>b</sup>	0.39	0.19	−0.88	−1.17	0.29	1.27
	$(\text{ClPh})_4\text{PPyH}_3$ 2	0.92	0.86 <sup>b</sup>	0.68 <sup>b</sup>	0.41	0.27	−0.83	−1.13	0.30	1.24
	$(\text{Cl}_2\text{Ph})_4\text{PPyH}_3$ 3	1.72	1.02 <sup>b</sup>	0.78 <sup>b</sup>	0.53	0.25	−0.77	−1.15	0.38	1.30

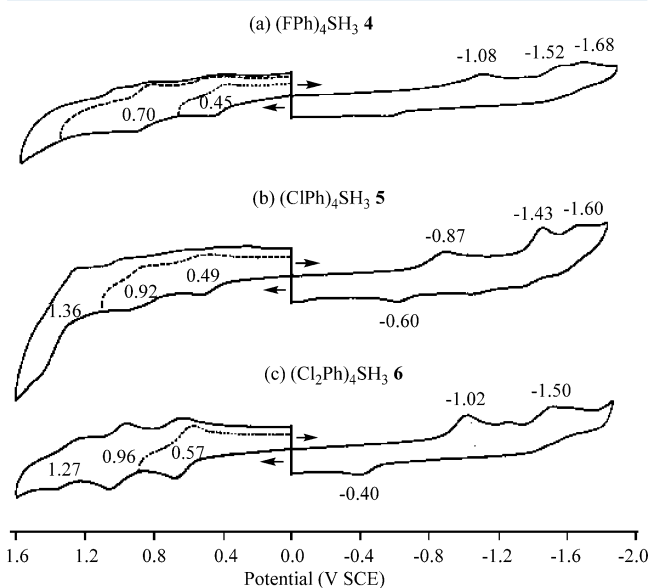
<sup>a</sup>Hammett substituent constant, see ref 64. <sup>b</sup>Irreversible peak potential at a scan rate of 0.10 V/s. <sup>c</sup>Potential difference between the second and first oxidations. <sup>d</sup>Potential difference between the first and second reductions. <sup>e</sup>The potential difference between the first oxidation and first reduction.



**Figure 6.** Thin-layer UV–visible spectral changes of  $(\text{Cl}_2\text{Ph})_4\text{PPyH}_3$  **3** during the controlled potential (a) reductions and (b) oxidations in  $\text{CH}_2\text{Cl}_2$  containing 0.1 M TBAP.

lower part of Figure 6b and were not investigated further in the present study.

**Electroreduction of Sapphyrins.** The redox properties of sapphyrins **4–6** were also examined in PhCN containing 0.1 M TBAP. Cyclic voltammograms of these compounds are shown in Figure 7, and the half-wave potentials are summarized in Table 5.



**Figure 7.** Cyclic voltammograms of sapphyrins **4–6** in PhCN containing 0.1 M TBAP. Scan rate = 0.10 V/s.

While the open-chain pentapyrroles exhibit reversible reductions in PhCN (Supporting Information, Figure S2), the reductions of the sapphyrins are irreversible under the same solution conditions (Figure 7). The first reduction occurs at  $E_{\text{pc}} = -0.87$  to  $-1.08$  V (depending upon the specific compound) while the second and third reductions are located between  $-1.43$  and  $-1.68$  V vs SCE. As will be demonstrated, the first reduction of  $(\text{Ar})_4\text{SH}_3$  involves a following chemical reaction

and formation of the deprotonated species  $[(\text{Ar})_4\text{SH}_2]^-$  as a final product of the initial one-electron reduction. The anionic product of this electrochemical EC mechanism can then be oxidized by one-electron on a return scan to give  $(\text{Ar})_4\text{SH}_2$  or it can be stepwise reduced by two electrons to give  $[(\text{Ar})_4\text{SH}_2]^{2-}$  and of  $[(\text{Ar})_4\text{SH}_2]^{3-}$  at more negative potentials. The electrogenerated products,  $[(\text{Ar})_4\text{SH}_2]^{2-}$  and  $[(\text{Ar})_4\text{SH}_2]^{3-}$ , are only moderately stable by cyclic voltammetry and show several anodic oxidation peaks on the return scan. This is illustrated in Figure 8 for the case of  $(\text{ClPh})_4\text{SH}_3$  **5**. This proposed mechanism is shown in Scheme 3 and is similar to what has been reported for the reduction of free-base corroles under similar solution conditions.<sup>66</sup>

Evidence for the formation of  $[(\text{Ar})_4\text{SH}_2]^-$  after the addition of one electron to  $(\text{Ar})_4\text{SH}_3$  comes from thin-layer spectroelectrochemistry of the type shown in Figure 9a for  $(\text{ClPh})_4\text{SH}_3$  **5**. As seen in this figure, the Soret and Q bands of **5** decrease in intensity during controlled potential reduction at  $-1.00$  V as new bands grow in at 514, 732, and 805 nm. The final spectrum of this reduction is almost exactly the same as the spectrum of the unreduced compound obtained in PhCN containing 2.0 equiv of added TBAOH (see Figure 10). This result is consistent with the electrochemistry and the conversion of  $(\text{ClPh})_4\text{SH}_3$  to  $[(\text{ClPh})_4\text{SH}_2]^-$  by addition of base or by electroreduction. Similar UV–visible spectra are also seen for the other two sapphyrins after reduction or after addition of base to solutions of the neutral compound (see Figure 10).

The spectral changes which occur during the second controlled potential reduction of  $(\text{ClPh})_4\text{SH}_3$  **5** at  $-1.50$  V actually correspond to a conversion of  $[(\text{ClPh})_4\text{SH}_2]^-$  to  $[(\text{ClPh})_4\text{SH}_2]^{2-}$  (Process II in Scheme 3).

**Electrooxidation of Sapphyrins.** Up to three reversible one-electron oxidations are observed for each sapphyrin in PhCN. The first oxidation ranges from  $E_{1/2} = 0.45$  V for compound **4** to  $0.57$  V for compound **6** while the second oxidation ranges from  $E_{1/2} = 0.70$  V for **4** to  $0.96$  V for **6** (see Table 5). The difference in half-wave potentials between the first and the second oxidations are listed in Table 5 and amounts to 0.25 V for **4**, 0.43 V for **5** and 0.39 V for **6**,

Table 5. Half-Wave Potentials (V vs SCE) of Substituted Sapphyrins in PhCN, 0.1 M TBAP

compound	4σ <sup>a</sup>	oxidation				reduction			HOMO–LUMO gap (V) <sup>d</sup>
		third	second	first	ΔE(2o-1o) <sup>b</sup>	first	second	third	
(FPh) <sub>4</sub> SH <sub>3</sub> 4	0.24		0.70	0.45	0.25	−1.08 <sup>c</sup>	−1.52 <sup>c</sup>	−1.68 <sup>c</sup>	1.35
(ClPh) <sub>4</sub> SH <sub>3</sub> 5	0.92	1.36	0.92	0.49	0.43	−0.87 <sup>c</sup>	−1.43 <sup>c</sup>	−1.60 <sup>c</sup>	1.36
(Cl <sub>2</sub> Ph) <sub>4</sub> SH <sub>3</sub> 6	1.72	1.27	0.96	0.57	0.39	−1.02 <sup>c</sup>	−1.50 <sup>c</sup>		1.59

<sup>a</sup>Hammett substituent constant, see ref 64. <sup>b</sup>Potential difference between the second and first oxidations. <sup>c</sup>Irreversible peak potential at a scan rate of 0.10 V/s. <sup>d</sup>The potential difference between the first oxidation and first reduction.

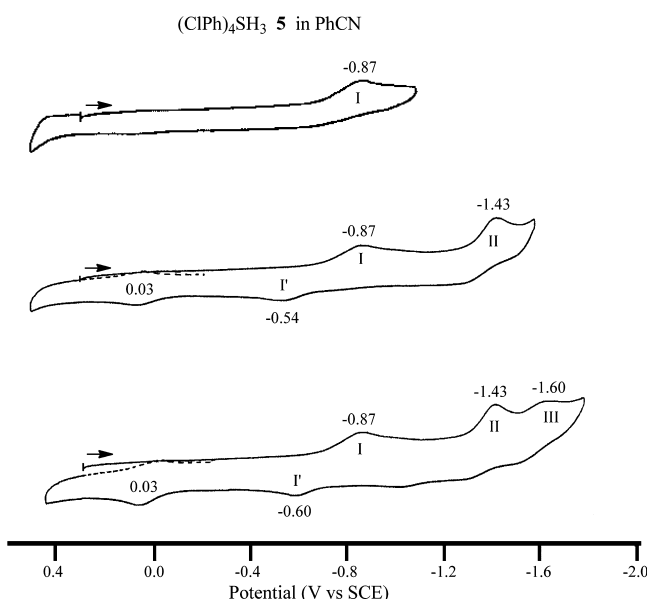
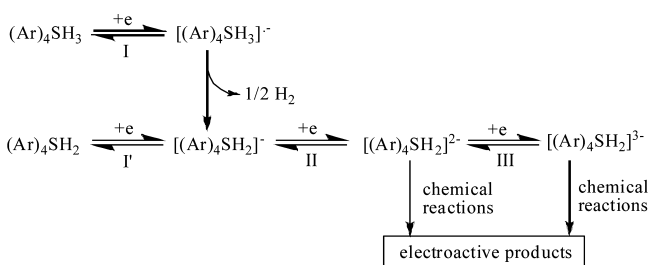


Figure 8. Cyclic voltammograms illustrating the reductions of (ClPh)<sub>4</sub>SH<sub>3</sub> 5 in PhCN containing 0.1 M TBAP. Scan rate = 0.10 V/s.

### Scheme 3. Reduction Mechanism of Sapphyrins in PhCN Containing 0.1 M TBAP



respectively. Similar values of  $\Delta E_{1/2}$  were measured for two of the three related open-chain pentapyrroles, namely, **1** ( $\Delta E_{1/2} = 0.27$  V) and **3** ( $\Delta E_{1/2} = 0.39$  V) (Table 4). A bigger difference occurs between compound **2** and **5** where  $\Delta E_{1/2} = 0.23$  and 0.42 V, respectively.

Thin-layer UV–visible spectral changes of each sapphyrin were measured during the first and second controlled-potential oxidations in PhCN containing 0.1 M TBAP. As seen in Figure 9b for compound **5**, the Soret and Q bands both decrease in intensity during the two stepwise oxidations, suggesting formation of a  $\pi$ -cation radical and dication, respectively. The spectral changes in each oxidation step are reversible, and consistent with a stable oxidation product being formed under the given experimental conditions.

It should be pointed out that the investigated sapphyrins are both easier to reduce and easier to oxidize than structurally

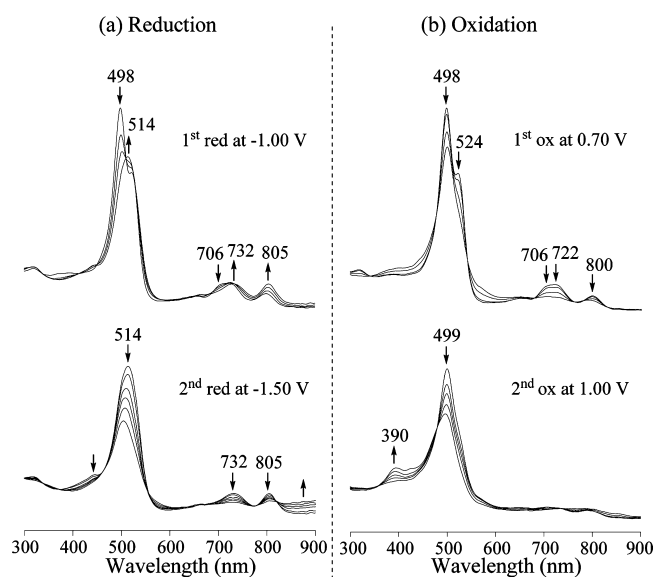
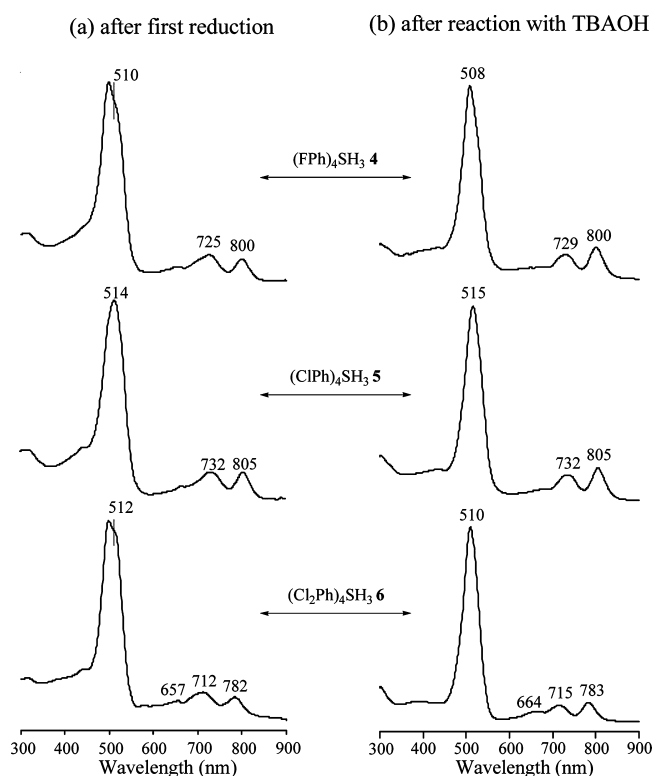


Figure 9. Thin layer UV–visible spectral changes of (ClPh)<sub>4</sub>SH<sub>3</sub> 5 during controlled potential (a) reductions and (b) oxidations in PhCN containing 0.1 M TBAP.

related porphyrins with similar substituents. A true thermodynamic HOMO–LUMO gap cannot be determined for the sapphyrins because of the irreversible first reduction. However, it is still important to point out that the measured separation between the first reduction and the first oxidation of the sapphyrins **4** and **5** (1.35 and 1.36 V, respectively) is almost identical to the electrochemically measured HOMO–LUMO gap of the open-chain pentapyrroles **1** and **2** (1.32 and 1.31 V). All four values are substantially less than for free-base porphyrins where the HOMO–LUMO gap averages about 2.25 V in nonaqueous media.<sup>63</sup>

In conclusion, the open-chain pentapyrroles undergo two reversible one-electron reductions and two reversible one-electron oxidations to generate  $[(Ar)PPyH_3]^-$ ,  $[(Ar)PPyH_3]^{2-}$ ,  $[(Ar)PPyH_3]^+$ , and  $[(Ar)PPyH_3]^{2+}$  in nonaqueous media. The corresponding sapphyrins exhibit two or three reversible one-electron oxidations in PhCN, but the reductions of these compounds are irreversible because of coupled chemical reactions following electron transfer. Very similar UV–visible spectra are seen after controlled potential oxidation of the open-chain pentapyrroles in CH<sub>2</sub>Cl<sub>2</sub> and after addition of TFA to the neutral compounds in the same solvent, suggesting that protonation reactions are occurring in both cases. These kinds of oxidation-induced protonation reactions have previously been reported for other open chain oligopyrrole systems as well as for oxidized free-base corroles and oxidized free-base porphyrins.





**Figure 10.** Spectra of sapphyrins obtained (a) after the first controlled potential reduction and (b) after the reaction with 2.0 equiv of TBAOH in PhCN.

## ■ ASSOCIATED CONTENT

### Supporting Information

Neutral UV–visible spectra of open-chain pentapyrroles **1–3** and sapphyrins **4–6** in  $\text{CH}_2\text{Cl}_2$  and cyclic voltammograms of the compounds **1–3** in PhCN containing 0.1 M TBAP. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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### Notes

The authors declare no competing financial interest.

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