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Meso-aryl substituted free-base tripyrrins: preparation and electrochemically induced protonation/deprotonation reactions. Single crystal X-ray analysis of (2,6-difPh)\textsubscript{2}TriPyH

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Three meso-substituted pyrrole-terminated tripyrrins were isolated for the first time as side products in the synthesis of triarylcorroles and characterized by spectroscopic and electrochemical techniques. The examined compounds are represented as \( (\text{Ar})\text{TriPyH} \), where the TriPy is the conjugated tripyrrin monoanion and \( \text{Ar} \) a 2,6-difPh, 2,6-dicPh or 2,4-dicPh substituent. A single crystal X-ray structure of (2,6-difPh)\textsubscript{2}TriPyH is also presented. This is the first X-ray structure of a meso-aryl substituted tripyrrin. Each tripyrrin undergoes two reductions and three oxidations in CH\textsubscript{2}Cl\textsubscript{2}. The first one electron addition and first one-electron abstraction lead to formation of \( \pi \)-anion and \( \pi \)-cation radicals with a potential separation between the two processes of 1.71 to 1.76 V. However, both electrogenerated products are unstable and undergo a rapid chemical reaction to give new electroactive species which are identified as the deprotonated and protonated compounds, respectively. The reaction products were characterized by spectroelectrochemistry and comparisons are made with spectroscopic data obtained during base and acid titrations in CH\textsubscript{2}Cl\textsubscript{2}.

The diprotonated form of \( \beta \)-substituted tripyrrins has been characterized in solution by NMR spectroscopy\textsuperscript{13,16-18} and one free-base \( \beta \)-substituted tripyrrin has been structurally characterized.\textsuperscript{23} However, almost nothing is known about free-base meso-substituted tripyrrins due to the instability of these compounds.\textsuperscript{24}

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**Introduction**

Tripyrrins and the related tripyrranes (Chart 1) are intermediates in the synthesis of porphyrins\textsuperscript{1} and expanded porphyrins,\textsuperscript{2} which have been mentioned in the literature for over four decades.\textsuperscript{3-24} The tripyrrins can be considered as formally derived from the macrocyclic parent porphyrins by the loss of one of the four pyrrole rings\textsuperscript{3-12} and have potential applications in the field of coordination polymers\textsuperscript{20} and fluorescent materials.\textsuperscript{25,26} However, due to the high propensity of the non-metallated compounds to decompose in the presence of weak nucleophiles, their characterization in solution has been limited in large part to methyl terminated species,\textsuperscript{13} meso-oxo derivatives\textsuperscript{9} or stable tripyrrinones with enolizable terminal hydroxy functionalities.\textsuperscript{6,9,11,12}

![Chart 1 Structures of tripyrrin and tripyrrane.](image)

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**Scheme 1 Synthetic route for obtaining triarylcorroles, open-chain tetrapyrrines and the diaryltripyrins 1-3.**
The often used synthetic method for obtaining triarylcorroles leads to two major side products; one is an open-chain tetraarylpentapyrrole and the other a diaryltripyrpin which is formed in smaller quantities (see structures in Scheme 1). We recently isolated and electrochemically characterized a series of the open-chain tetraarylpentapyrrole side products\(^ {27,28}\) and have now turned our attention to the diaryltripyrpin side products, three of which were isolated and characterized in the present paper by \(^1\)H NMR and absorption spectroscopy, mass spectrometry, electrochemistry, and spectroelectrochemistry. Protonation and deprotonation reactions are also elucidated in nonaqueous media. The examined compounds are represented as \((\text{Ar})_2\text{TriPyH}\), where TriPy is a monoanion of the conjugated diaryltripyrpin and Ar is a 2,6-diClPh \((1)\), 2,6-diClPh \((2)\) or 2,4-diClPh \((3)\) substituent on the two \(\text{meso}\) positions of the compound. One of the compounds, \((2,6\text{-diFPh})\text{TriPyH}\), was also structurally characterized and, to our knowledge, is the first X-ray structure of a \(\text{meso}\)-substituted free-base open-chain tripyrrin.

Results and Discussion

Synthesis and Characterization

The diaryltripyrpins \(1-3\) shown in Scheme 1 were isolated with a yield ranging from 3 to 5%. Each compound was characterized by \(^1\)H NMR and absorption spectroscopy, mass spectrometry, electrochemistry and spectroelectrochemistry. The diaryltripyrins and open-chain tetraarylpentapyroles both contain five pyrrole groups. However, as seen in Scheme 1, the diaryltripyrpin posses two \(\text{meso}\)-aryl groups rather than four as in the open-chain tetraarylpentapyrrole. The diaryltripyrpin also has two C-C single bands between two adjacent pyrroles at the both ends of the compound. This difference in structure leads to quite different UV-visible spectra for the two compounds.

![UV-visible spectra of neutral (a) open-chain pentapyrrole, (2,4-diClPh)\(2\)PPyH\(2\) and (b) the diaryltripyrpin, (2,4-diClPh)\(2\)TriPyH \(3\) in CH\(_3\)Cl\(_2\).](image1)

As previously reported,\(^ {27,28}\) UV-visible spectra of the openchain tetraarylpentapyroles are characterized in nonaqueous media by a split Soret-like band and two weak Q bands. An example is given in Figure 1a for (2,4-diClPh)\(2\)PPyH\(2\) which posses a split Soret-like band in CH\(_3\)Cl\(_2\) at 369 and 499 nm and two Q bands at 794 and 866 nm. The related diaryltripyrpin with two Cl\(_2\)Ph substituents, (2,4-diClPh)\(2\)TriPyH also has a split Soret-like band at 334 and 417 nm, but the band at 417 nm is three-times more intense than the band at 334 nm (Figure 1l). The diaryltripyrpin also has two overlapped Q bands centered at 619 and 675 nm. Similar absorption spectra are seen for compounds \(1\) and \(2\), with the most intense Soret-like band of the tripyrrin compound, being blue-shifted by \(-80\) nm and the Q bands blue-shifted by about 180-190 nm as compared to that of open-chain pentapyrrole having the same Ar groups. This difference in absorption spectra is consistent with the fact that the diaryltripyrins have a smaller conjugated \(\pi\)-system than the related open-chain tetraarylpentapyroles.

![\(^1\)H NMR spectrum of (2,6-diFPh)\(2\)TriPyH \(1\) in CD\(_2\)COCD\(_2\) at 298 K.](image2)

\(^1\)H NMR and H-H COSY NMR spectra of compounds \(1-3\) were measured in CD\(_2\)COCD\(_2\) or CD\(_3\)Cl\(_2\). Examples of spectra are shown in Figure 2 for (2,6-diFPh)\(2\)TriPyH \(1\), Figure S1 for (2,6-diClPh)\(2\)TriPyH \(2\) and Figure S2 for (2,4-diClPh)\(2\)TriPyH respectively. The three NH protons of \(1\) appear as two broad resonances at 13.40 and 9.84 ppm (Figure 2) and similar resonances are seen for \(2\) and \(3\) (Figures S1 and S2). The resonances of the phenyl protons are located between 7.22 and 7.70 ppm for \(1\) and at 7.56 to 7.71 ppm for \(3\) while resonances of the pyrrole-CH protons are located at 6.27 and 7.22 ppm for \(1\) and at 6.17 to 7.22 ppm for \(3\) (see Figures 3 and S3, respectively).

![H-H COSY NMR spectrum of (2,6-diFPh)\(2\)TriPyH \(1\) in CD\(_2\)COCD\(_2\).](image3)
X-ray crystal analysis

A single crystal of (2,6-diFPh)3TriPyH 1 was obtained by vapor diffusion of n-hexane into a CH2Cl2 solution. The crystal structure was unambiguously determined by single-crystal X-ray diffraction analysis (Figs 4, S4 and S5) while the crystallographic data and selected bond lengths and angles are summarized in Tables S1 and S2, respectively.

Although significant disorder is found for one of the terminal pyrroles, the structure of (2,6-diFPh)3TriPyH 1 is well-defined. The Py1 and Py2 share the same plane with a dihedral angle of 16.3° to Py3. Py1 and Py2 are inclined by 10.9° and 27.9° with respect to Py3. The average bond length between the meso-carbon atoms and the phenyl rings is 1.489 Å. The crystal structure confirms that compound 1 is a meso-substituted tripyrrin with two direct pyrrole-pyrrole linkages and is clearly helical in the solid state.

![Fig 4. Single crystal X-ray structures of 1 with thermal ellipsoids shown at the 50 % probability level. (a) the perspective view and (b) the side view with solvent molecule omitted for clarity.](image)

Protonation reactions

It was previously demonstrated that bi-, ter- and quarter-pyrroles as well as open-chain tetrapentapyroles can be protonated by addition of acid to CH2Cl2 solutions of the compounds. Protonations also occur for the currently examined diarylpyrrins. The relevant reaction is given in equation 1 and an example of the UV-vis spectral changes obtained during a titration of (2,6-diFPh)3TriPyH 1 with trifluoroacetic acid (TFA) in CH2Cl2 is illustrated in Figure 5.

\[
(Ar)_2\text{TriPyH} + 2H^+ \rightleftharpoons [(Ar)_2\text{TriPyH}_2]^{2+} \quad (1)
\]

The final spectrum of the diprotonated form of 1 is characterized by a Soret-like band at 459 nm and two broad Q-like bands at 678 and 739 nm. The slope of the Hill plot, shown as an insert in Figure 5, is 2.0, indicating a single step, addition of two protons to give [(2,6-diFPh)3TriPyH2]2+ as the final protonation product in solution. The protonation constant was calculated as logβ2 = 11.3 for compound 1 in CH2Cl2. Similar bis-protonation reactions occur for compounds 2 and 3 and the values of logβ2 were calculated as 11.8 and 10.9, respectively, under the same solution conditions. The logβ2 of 11.3 for compound 1 can be compared to a logβ2 = 11.0 for the addition of two protons to the open-chain tetraptentapyrrole containing four C6H4F meso-substituents.

![Fig 5. UV/Vis spectral changes of (2,6-diFPh)3TriPyH 1 during the titration with TFA in CH2Cl2, (insert showing the Hill plot used for calculating the number of added protons and equilibrium constant).](image)

Electrochemistry and spectroelectrochemistry

The (Ar)2TriPyH derivatives 1-3 are characterized by three oxidations and two reductions in CH2Cl2 but, as will be described on the following pages, a chemical reaction follows the first one-electron abstraction and first electron addition to give protonated and deprotonated products which are themselves electroactive as indicated in Scheme 2.

![Scheme 2. Proposed redox mechanism of (Ar)2TriPyH in CH2Cl2, 0.1 M TBAP.](image)

Evidence for the above mechanism and the products electron transfer are given by the combined results of cyclic voltammetry, spectroelectrochemistry and titrations of the neutral compounds with TFA or TBAOH. A good example of the chemical reactions coupled to the oxidations of 1-3 in CH2Cl2 is given by the cyclic voltammograms in Figure 6. The first one-
electron abstraction is irreversible and located at $E_{pa} = 0.83$ to 0.86 V for a scan rate of 0.10 V/s. This initial oxidation of the tripyrrins is followed by two addition oxidations at $E_{pa} = 0.98$-1.02 V and $E_{1/2} = 1.33$-1.35 V for a scan rate of 0.10 V/s. A new re-reduction process is also seen at $E_{1/2} = -0.10 \sim -0.13$ V. This process does not occur on initial positive scans from -0.40 to 0.60 V and is thus not associated with the neutral compound.

![Cyclic voltammograms showing the initial oxidations of (a) (2,6-diFPh)$_2$TriPyH 1, (b) (2,6-diClPh)$_2$TriPyH 2 and (c) (2,4-diClPh)$_2$TriPyH 3 and the associated oxidation and reduction of the diprotonated diaryltripyrin formed at the electrode surface in CH$_2$Cl$_2$, 0.1 M TBAP. Scan rate = 0.10 V/s.](image)

The spectrum is almost identical to the absorption spectrum for the diprotonated compound 1 in CH$_2$Cl$_2$, containing excess TFA (Figure 5) which is characterized by major bands at 459, 678 and 739 nm plus a shoulder band at 480 nm. The product of the protonation in Figure 5 is assigned as [(Ar)$_2$TriPyH]$_2$.

There is also a strong spectral similarity between the one-electron oxidation product of compounds 2 and 3 in CH$_2$Cl$_2$, 0.1 M TBAP and the diprotonated species formed after addition of two protons to the neutral diaryltripyrins in CH$_2$Cl$_2$. This is illustrated in Figure 8 where the neutral diaryltripyrins are shown by solid lines and the products of protonation and electrooxidation by dashed lines. Again, there is no doubt that the same species is formed in solution under both sets of experimental conditions.

![UV/Vis spectra of (a) (2,6-diClPh)$_2$TriPyH 2 and (b) (2,4-diClPh)$_2$TriPyH 3 before and after the first oxidation in thin-layer cell in CH$_2$Cl$_2$ containing 0.1 M TBAP as well as before and after diprotonation by addition of TFA into the CH$_2$Cl$_2$ solution of the compound.](image)

Additional characterizations were not carried out to identify the products for oxidation or reduction of the diprotonated tripyrrins, but electrochemical monitoring of the species in solution during a titration with TFA showed the disappearance of the first two irreversible oxidation peaks at 0.83-0.86 V and 0.98-1.02 V, leaving only the processes at $E_0 = 1.33$ and -0.18 V. A cyclic voltammogram for compound 3 in CH$_2$Cl$_2$ containing two equivalents of TFA is shown in Figure S6 and the redox reactions are assigned to the oxidation and reduction of [(Ar)$_2$TriPyH]$_2$ as shown in Scheme 3.

![Proposed mechanism for oxidation induced protonation reactions of (Ar)$_2$TriPyH in CH$_2$Cl$_2$, 0.1 M TBAP. The listed potentials are for compound 3 (see Figure 6).](image)
This redox active species can be generated via two pathways, either directly by diprotonation of $(Ar)_2$TriPyH to give $[(Ar)_2$TriPyH]$^{3+}$ or via a series of reactions involving an initial one electron abstraction (at 0.83 V for compound $3^3$) followed by diprotonation to give $[(Ar)_2$TriPyH]$^{3+}$ and then immediate back reduction to give $[(Ar)_2$TriPyH]$^{2+}$ as illustrated in the scheme. Similar oxidation-induced protonation reactions have previously been reported for the related open-chain oligopyrroles$^{30-33}$ as well as for free-base corroles$^{34-36}$ and free-base porphyrins.$^{37-39}$

The first one-electron oxidation of 1-3 is assigned to occur at the conjugated $\pi$-system of the tripyrrin and this is also the proposed site of the first irreversible one-electron reduction which occurs at a peak potential of -0.86 to -0.91 V as shown in Figure 9. This process is then followed by a second quasi-reversible one-electron reduction at $E_{pc} = -1.20$ to -1.23 V for a scan rate of 0.10 V/s. The second reduction is assigned to a reaction involving deprotonated tripyrrin as evidenced by comparison of the absorption spectrum after controlled potential reduction and the spectrum obtained after addition of TBAOH to the neutral compound. Examples of this spectral comparison is shown in Figure 10 where the species in solution after controlled potential reduction at -1.00 V is characterized by bands at 459, 698 and 765 nm in CH$_2$Cl$_2$, 0.1 M TBAP (Figure 10a) and an almost identical spectral pattern is seen after addition of TBAOH to solution to give the deprotonated compound.

Fig 9. Cyclic voltammograms showing the reductions of (a) (2,6-diFPh)$_2$TriPyH $1$, (b) (2,6-diClPh)$_2$TriPyH $2$ and (c) (2,4-diClPh)$_2$TriPyH $3$ in CH$_2$Cl$_2$, 0.1 M TBAP. Scan rate = 0.10 V/s.

The second reduction of 1-3 was also characterized in the thin-layer cell and the absorption spectrum for this species is shown in Figure 10b for the case of compound 1. The quasi-reversible redox process is associated with the addition of one-electron to the deprotonated dianion tripyrrin as shown by the proposed mechanism in Scheme 4 where the loss of one proton occurs upon addition of TBAOH to generate the anion deprotonation product $[(Ar)_2$TriPy] which can be reduced by one electron to give $[(Ar)_2$TriPy]$^2$.

Scheme 4. Proposed mechanism for reduction induced deprotonation of $(Ar)_2$TriPyH in CH$_2$Cl$_2$, 0.1 M TBAP. The listed potentials are for compound 1 in the absence of added base.
Additional confirmation of the mechanism shown in Scheme 4 is given by electrochemically monitoring the product obtained during a titration with TBAOH. An example of the data obtained is given in Figure 11 for the case of 1. As the base concentration is increased from 1 to 12 equivalents, the currents for the initial reduction peak at $E_p = -0.87$ V decrease in magnitude while currents for the second reduction peak increase slightly. After 12 equivalents of TBAOH have been added to solution only the second reduction remains and this is consistent with a conversion [[Ar$_2$TriPy]$^\cdot$] to [[Ar$_2$TriPy]$^\cdot$]. However, it should be noted that the re-oxidation peak potential of [[Ar$_2$TriPy]$^\cdot$] varies as a function of base concentration in solution, shifting from $E_p = -0.99$ V in CH$_2$Cl$_2$, 0.1 M TBAH to $E_p = -0.89$ V in solutions of CH$_2$Cl$_2$ containing 12 equivalents of base. This suggests the presence of a coupled chemical reaction associated with the re-oxidation but further examination of this process was not undertaken and is beyond the scope of the present study.

**Experimental Section**

**Instrumentation**

$^1$H NMR spectra were recorded on Bruker Avance II 400 MHz or Bruker DRX500 at 298K. MALDI-TOF mass spectra were taken on a Bruker BIFLEX III ultra-high resolution with alpha-cyano-4-hydroxycinnamic acid as the matrix. Electronic absorption spectra were recorded with a Hewlett-Packard Model 8453 diode array spectrophotometer.

Electrochemical measurements were carried out at 298K using a CHI-730C Electrochemistry Workstation. A homemade three-electrode cell was used for cyclic voltammetric measurements and consisted of a 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 spectrophotometric experiments were performed with a home-built thin-layer cell which has a light transparent platinum networking electrode. Potentials were applied and monitored with an EG&G PAR Model 173 potentiostat or a BiStat electrochemistry station. Time-resolved UV-visible spectra were recorded with a Hewlett-Packard Model 8453 diode array spectrophotometer. High purity N$_2$ was used to deoxygenate the solution and was kept over the solution during the electrochemical and spectrophotometric experiments.

**Chemicals**

All solvents and chemicals were purchased from Sinopharm Chemical Reagent Co. or Aldrich Chemical Co. and used as received. Tetra-n-butylammonium perchlorate (TBAP) was purchased from Sigma-Aldrich Co. and used as received.

**Isolation of [Ar$_2$TriPyH] from synthesis of triarylcorroles**

Substituted aldehyde (5 mmol) and pyrrole (25 mmol, 1.73 mL) were dissolved in CH$_2$OH (20 mL), after which HCl (2.0 mL conc. HCl in 60 mL H$_2$O) was slowly poured into the flask and the solution stirred at room temperature for 45 min. The reaction product was extracted with CH$_2$Cl$_2$, the organic layer washed twice with NaHCO$_3$ and twice with H$_2$O, after which it was
was dried with Na₂SO₄, filtered, and then diluted to 200 mL with CH₂Cl₂. p-Chloranil (1.23 g, 5 mmol) was added to the solution which was then refluxed for 2h. The reaction mixture was passed over a silica column using CH₂Cl₂ as eluent. The first purple-red color fraction mainly contained triarylcrores and open-chain pentapyrroles. The following green fractions contained the target molecules and were collected for further purification. After evaporation of the solvent, the concentrated mixture was purified several times by chromatography on a silica column using CH₂Cl₂/hexane as eluent to give the desired diarylpyrrenes.

(2,6-difPh₃)₃TriPyH (1). Yield: 73 mg, 5%; UV-vis (CH₂Cl₂): λ max (nm (ε×10⁴ M⁻¹ cm⁻¹)) 335 (1.85), 416 (4.67), 620 (0.97) and 671 (1.02); 1H NMR (400 MHz, acetone): δ = 13.40 (br, s, 1H, N-H of Py3), 9.84 (br, s, 2H, N-H of Py1 and Py5), 7.70-7.63 (m, 2H, p-H of Ph-H), 7.26 – 7.24 (m, 4H, Ph-H), 7.22 (2, 2H, β-H of Py2), 7.00 (2, 2H, α-H of Py1 and Py5), 6.93 (d, J = 4.7 Hz, 2H, β-H of Py4), 6.35-6.33 (m, 2H, β-H of Py3), 6.29 (d, J = 8.5 Hz, 4H, β-H of Py1 and Py5); [MALDI-TOF]: m/z calculated for C₃₅H₃₇F₃N₅ 575.173; found: 575.141.

(2,6-dicPh₂)₃TriPyH (2). Yield: 50 mg, 3%; UV-vis (CH₂Cl₂): λ max (nm (ε×10⁴ M⁻¹ cm⁻¹)) 334 (2.38), 417 (5.95), 617 (1.25) and 669 (1.35); 1H NMR (400 MHz, CDCl₃): δ = 13.52 (br, s, 1H, N-H of Py3), 9.01 (br, s, 2H, N-H of Py1 and Py5), 7.56-7.54 (m, 4H, Ph-H), 7.47-7.43 (m, 2H, Ph-H), 7.12 (d, J = 4.6 Hz, 2H, β-H of Py2), 6.92 (m, 2H, α-H of Py1 and Py5), 6.82 (d, J = 4.6 Hz, 2H, β-H of Py4), 6.44-6.42 (m, 2H, β-H of Py3), 6.16-6.13 (m, 4H, β-H of Py1 and Py5); [MALDI-TOF]: m/z calculated for C₃₄H₃₅F₂N₅ 641.052; found: 641.001.

(2,6-dicPh₁)₃TriPyH (3). Yield: 45 mg, 3%; UV-vis (CH₂Cl₂): λ max (nm (ε×10⁴ M⁻¹ cm⁻¹)) 334 (1.61), 417 (4.09), 619 (1.47) and 675 (1.56); 1H NMR (400 MHz, acetone): δ = 13.36 (br, s, 1H, N-H of Py3), 7.98 (br, s, 2H, N-H of Py1 and Py5), 7.71-7.70 (m, 2H, Ph-H), 7.61-7.56 (m, 4H, Ph-H), 7.22 (d, J = 4.6 Hz, 2H, β-H of Py2), 6.97 (d, J = 1.7 Hz, 2H, α-H of Py1 and Py5), 6.82 (d, J = 4.6 Hz, 2H, β-H of Py4), 6.32-6.29 (m, 4H, β-H of Py1 and Py5), 6.19 (d, J = 6.3 Hz, 2H, β-H of Py3); [MALDI-TOF]: m/z calculated for C₃₃H₃₄F₂N₅ 641.376; found: 640.704.

X-ray Crystallography of (2,6-difPh₃)₃TriPyH

A crystal of (2,6-difPh₃)₃TriPy was obtained by slow diffusion of n-hexane into a dichloromethane solution containing the compound and placed on a glass fiber for data collection. Diffraction data was collected on a Rigaku Saturn 724 CCD area detector diffractometer, equipped with graphite monochromatized Mo Kα (λ = 0.71070 Å) radiation at 153(2) K. The crystal structure was solved by direct methods using difference Fourier synthesis with SHELXTL97, and refined by full matrix least squares method. The N-H hydrogen was located from difference electron density maps and the C-H hydrogens were placed in calculated positions and refined with a riding model.

Determination of protonation constants

A series of CH₂Cl₂ solutions containing trifluoroacetic acid (TFA) in different concentrations was prepared and used as an acid-titration reagent. Microliter quantities of TFA in CH₂Cl₂ were added gradually to a 5.0 mL CH₂Cl₂ solution of the diarylpyrren in a 1.0 cm cell, and the spectral changes were monitored after each addition. Changes in UV-visible spectra during the titration with TFA were analyzed as a function of the concentration of added acid using the Hill equation to calculate equilibrium constants for proton addition in the nonaqueous solvent, CH₂Cl₂.

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Notes and references

29. CCDC 1417683 of 1 contains the supplementary crystallographic data which can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.com.ac.uk/data_request/cif.
Synopsis

*Meso*-aryl substituted free-base tripyrrins: preparation and electrochemically induced protonation/deprotonation reactions. Single crystal X-ray analysis of (2,6-diFPh)₃TriPyH

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Three *meso*-substituted free-base tripyrrins were successfully isolated as side-products from the synthesis of triarylcorroles. The electrochemical properties as well as the protonation-deprotonation reactions of the tripyrrin were examined in nonaqueous media. One of the compounds was also characterized by X-ray crystallographic analysis.