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26π Aromatic Core-Modified Hexaphyrins: Syntheses, Characterization, and Structural Diversities

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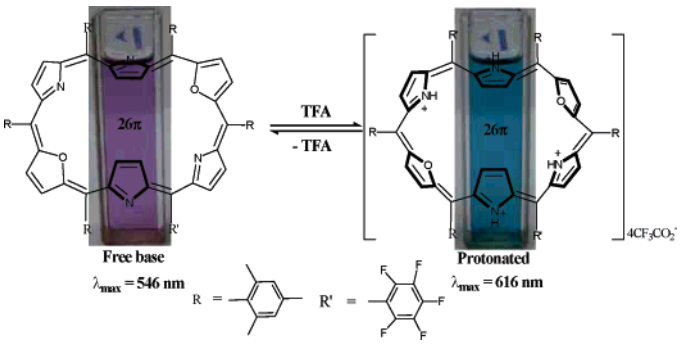

Synthesis and characterization of several 26π core-modified hexaphyrins are reported. The synthetic methodology involved a well-known acid-catalyzed MacDonald-type condensation reaction of the required tripyrrane with electron deficient pentafluorobenzaldehyde. The nature of the product and yield depends on the nature of the acid catalyst and its concentration. Dioxahexaphyrin **9** was isolated only when 0.5 equiv of TFA was used as a catalyst, while dithiahexaphyrin **10** and diselenahexaphyrin **11** were formed with TFA, PTSA, and even in the absence of catalyst. The detailed ^{1}H and 2-D COSY as well as HSQC experiments reveal the solution structure as well as the conformational mobility of hexaphyrins. In the tetracationic state, **10** and **11** exhibit a four heterocyclic ring inverted structure, while only two completely inverted heterocyclic rings were observed for **9**. The other four heterocyclic rings are only partially inverted in **9**. All the hexaphyrins reported here show aromatic character inferred from large $\Delta\delta$ values (difference in chemical shift between the most shielded and the most deshielded protons). Electronic absorption spectral studies also support the conformational changes observed upon protonation.

Introduction

Recently expanded porphyrins have attracted considerable attention because of their diverse applications.[1] Expanded porphyrins have more than 18π electrons in the conjugated pathway either due to an increased number of heterocyclic rings or due to multiple meso carbon bridges. Hexaphyrin is a class of expanded porphyrin in which six pyrrole/heterocyclic rings are linked in a cyclic fashion through meso carbon bridges.[2] Depending on the number of meso links, the hexaphyrin systems known are amethyrin (1.0.0.1.0.0),[3a] rosarin (1.0.1.0.1.0),[3b] rubyrin (1.1.0.1.1.0),[3c] hexaphyrin (1.1.1.1.1.1),[3d] and cyclo [6]

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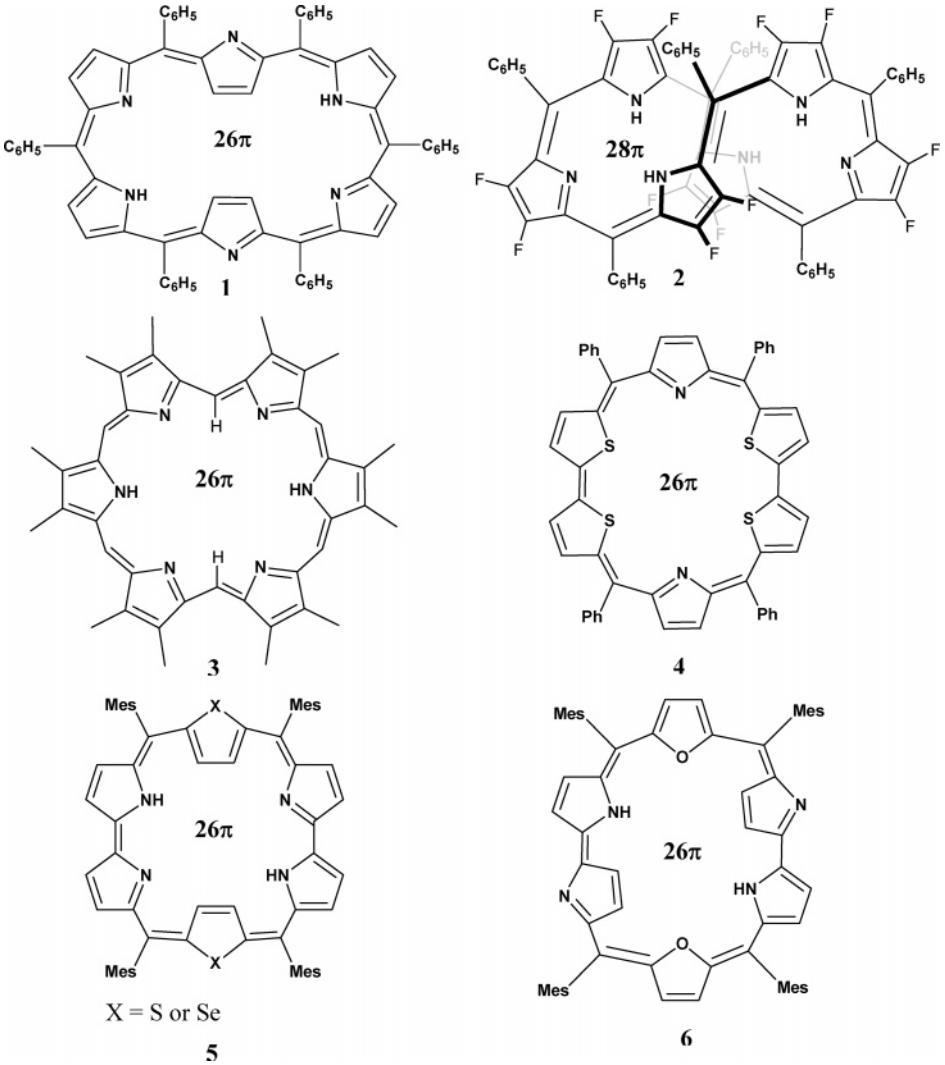
CHART 1



pyrrole.[3e] Hexaphyrin (1.1.1.1.1.1) **1** can be regarded as a real homologue of porphyrin in terms of a conjugated cyclic π-system with an alternate arrangement of heterocyclic rings and methine bridges. Hexaphyrins reported in the literature (Chart 1) were found to exhibit a regular structure as in **3**, inverted as in **1** (aromatic), as well as a figure eight conformation in **2** (nonaromatic). Core modification by substituting one or more pyrrole rings by furan, thiophene, and selenophene gives rise to macrocycles with modified electronic structures and properties.[4a] In this connection, the author's laboratory has reported several core-modified rubyrins that exhibit both regular (**4**) as well as inverted (**5** and **6**) structure.[4] Most of the hexaphyrins reported in the literature contain the same meso substituent, while there are a few reports on hexaphyrin with two different meso substituents.[5] In a recent paper,[6] we reported a one-pot synthesis of aromatic 26π dithiahexaphyrin and diselenahexaphyrin with two different meso substituents through acid-catalyzed MacDonald-type condensation of modified tripyrrane and sterically congested aldehyde. Modification of 26π hexaphyrins can alter the physical properties significantly.

There are few literature reports where hexaphyrins can be modified chemically through nucleophilic addition and substitution reactions.[7] However, the direct introduction of a different aromatic moiety at meso positions of hexaphyrin is more attractive as it can influence the electronic and optical properties significantly.[8] In this paper, we wish to report the synthesis of core-modified hexaphyrins via condensation reactions of appropriate precursors in the presence of appropriate catalysts. It has been shown that hexaphyrin exhibits a rich structural diversity where different ring inversions have been characterized through detailed ^{1}H and 2-D NMR studies. These ring inversions depend on the state of protonation and the nature of the heteroatom present in the hexaphyrin cavity.

Results and Discussion

Syntheses. Most of the hexaphyrins reported in the literature were synthesized either through a modified Rothenmund reac-

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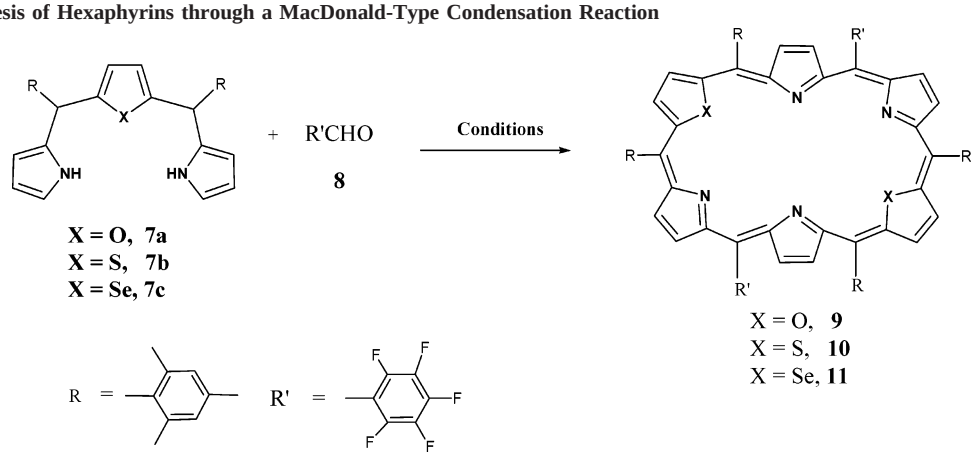
TABLE 1. Synthesis of Hexaphyrins through a MacDonald-Type Condensation Reaction



entry	conditions	X	yield (%)
1	0.5 equiv of PTSA	O	no reaction
2	0.5 equiv of PTSA	S	6.7
3	0.5 equiv of PTSA	Se	5
4	0.5 equiv of TFA	O	3.6
5	0.5 equiv of TFA	S	16
3	0.5 equiv of TFA	Se	7.2
7	no catalyst	O	no reaction
8	no catalyst	S	10
9	no catalyst	Se	7.6

tion[9] or through acid-catalyzed condensation of dipyrromethane with aromatic aldehydes.[10] In these methodologies, generally, multiple products are isolated leading to tedious purification procedures and lower yields. Furthermore, the hexaphyrins isolated were sensitive to reaction conditions. For example, Cavalerio and co-workers using a mixture of glacial acetic acid and nitrobenzene isolated both reduced and oxidized forms.[9c] On the other hand, Osuka and Anderson have independently reported a [2 + 2 + 2] condensation reaction of dipyrromethane with various aldehydes leading to the formation of desired hexaphyrins in addition to the porphyrins as the byproduct.[5] Interstingly, Osuka and co-workers isolated a 26π aromatic planar hexaphyrin using protic acid as a catalyst, while Anderson and co-workers isolated a reduced form 28π nonaromatic hexaphyrin using a Lewis acid as the catalyst. Thus, it is clear that the synthetic method where the desired hexaphyrins can be isolated as a single product is lacking in the literature, and development of such a methodology leads to the isolation of hexaphyrin in better yields, making them amenable for further studies for various applications.

A recent preliminary report from this laboratory describes the synthesis of aromatic core-modified hexaphyrin using a MacDonald-type condensation reaction of appropriate precursors.[6] The advantage of this methodology is the isolation of a single desired product avoiding the separation problems. In continuation of this study, in this paper, we have extended this methodology to various tripyrranes[11] containing the hetero atoms oxygen, sulfur, and selenium. The general synthetic protocol involves acid-catalyzed condensation of stable precursors containing heterocyclic rings such as furan, thiophene, and selenophene (i.e., oxa-tripyrrane **7a**, thia-tripyrrane **7b**, and selena-tripyrrane **7c** with pentafluorobenzaldehyde **8**). We have carefully studied the effect of nature and concentration of the catalyst on the yield of the resultant product. To understand the role of the acid catalyst in the condensation reaction, we have carried out the reaction under the following categories: (a) use of different acids of different acidities, for example, trifluoroacetic acid (TFA) and paratoluenesulphonic acid (PTSA) and (b) without the use of acid. This idea is based on a recent literature report on the noncatalyzed reaction of pyrrole and aldehyde leading to the formation of corroles.[12] The results of these studies are tabulated in Table 1. For example, the use of 0.5 equiv of PTSA as the acid catalyst resulted in the formation of both dithiahexaphyrin **10** and diselenahexaphyrin **11** in 6.7 and 5% yield, respectively. However, under this condition, **9** was not formed. This observation suggests that the reactivities of tripyrranes (**7**) are different under the reaction conditions. The fact that **9** was not formed with the PTSA catalyst prompted us to try the same reaction using an acid catalyst of higher acidity. Thus, using 0.5 equiv of TFA as a catalyst, dioxahexaphyrin **9** was isolated in 3.6% yield. Under this condition, tripyrranes **7b** and **7c** also gave the corresponding hexaphyrin **10** and **11** in 16 and 7.2% yield, respectively. It is known that the condensation reaction between pyrrole and electron with-

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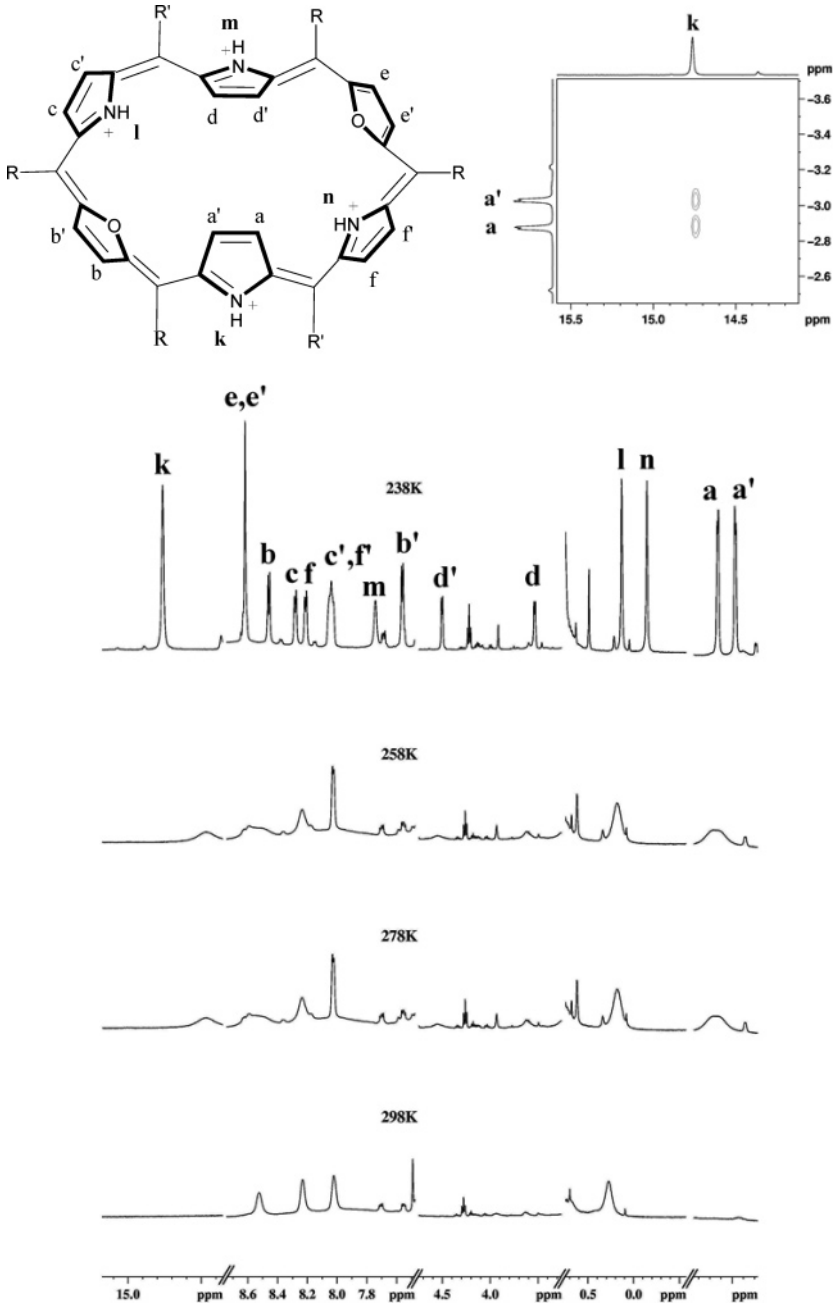


FIGURE 1. Temperature-dependent ^{1}H NMR spectra of completely protonated form of **9** in CD_2Cl_2, assignments are marked. The correlation observed for a and a′ protons with k proton in 2-D COSY is shown in the inset.

drawing aldehydes gives the corresponding corrole without the use of any acid catyalyst.[12] When we tried the reaction between tripyrrane and pentafluorobenzaldehyde in the presence of DDQ as oxidant, we were able to isolate 10 and 7.6% of **10** and **11**, while **9** was not formed under this condition because of the lower reactivity.

Increasing the acid concentration to 1 and 2 equiv decreased the yield of the desired product in all cases to almost 1% due to the acidolysis of tripyrranes in high acid concentration. In all cases, doubling the aldehyde concentration did not alter the percentage yield. After trying this procedure with protic acid, the effect of the Lewis acid on the cyclization process was also explored. There is a report in the literature on the formation of hexaphyrin along with other side products by Lewis acid-catalyzed condensation reactions.[9] The reaction of the modified tripyrranes (**7a**−**7c**) with aldehyde **8** using Lewis acids like BF_3·-OEt_2 and $SnCl_4$ did not yield any desired hexaphyrin in the present study.

NMR Studies. The proposed composition and the solution structures of the hexaphyrins (**9**−**11**) were found by the FAB mass and detailed ^{1}H and 2-D NMR studies on the free base as well as protonated derivatives. As expected, the hexaphyrins were found to be extremely conformationally mobile, and the proton NMR spectra could not be resolved at room temperature. The ^{1}H NMR spectra of hexaphyrins was found to be temperature dependent. Even at a low temperature of 218 K, the ^{1}H NMR of the free base exhibits only broad signals, and hence, assignment was done on the basis of 2-D COSY and HSQC

experiments. However, protonation of the hexaphyrin yields tetracationic species and efficiently arrests the fluxionality of the rings. Only after lowering the temperature in the range of 238−218 K was it possible to obtain fairly well-resolved spectra with sharp NH resonances and hence make the assignment possible. Interestingly, **10** and **11** behave similarly, while **9** shows different NMR behavior.

Figure 1 shows temperature-dependent ^{1}H NMR spectra of tetracationic dioxahexaphyrin **9**, and the assignments based on ^{1}H−^{1}H COSY and HSQC is marked in the spectrum (see Supporting Information for the COSY and HSQC spectrum). In the figure, 2-D COSY between 14.5−15.5 ppm is also included. Specifically, at 238 K, there are four different NH signals; two in the shielded region at 0.13 and −0.14 ppm and two in the deshielded region at 7.75 and 14.75 ppm. These assignments were based on the absence of any correlation with ^{13}C signals in HSQC spectrum. The chemical shifts of NH signals suggest that the two pyrrole rings in the shielded region are experiencing the ring current effect while the other two pyrrole rings are inverted and hence deshielded. The difference in the chemical shift of the two inverted rings suggests that the degree of inversion is not the same in both cases. This is further supported by the chemical shift of β-protons a and a′ and d and d′. The a and a′ protons resonate at −2.87 and −3.03 ppm, while the d and d′ protons resonate at 3.54 and 4.50 ppm. Furthermore, the corresponding NH protons (k and m) of these pyrrole rings are correlated with β-protons a and a′ and d and d′, respectively, confirming the assignments. The furan ring β-protons (b and b′ and e and e′) resonate as four doublets at 8.46, 7.57, and 8.62 ppm, and they show correlation in ^{1}H−^{1}H COSY between themselves, confirming the assignments.

The remaining four pyrrole protons (c and c′ and f and f′) resonate at 8.28 and 8.03 and 8.22 and 8.03 ppm and show correlation between themselves. The aromatic nature of the macrocycle is clearly reflected in the difference in chemical shift $\Delta\delta$ of the outer NH proton (14.75) and inner ring β-proton (−3.03), which is 17.78.

A comparison of the ^{1}H NMR spectra of the free base of **9** and it's fully protonated form also revealed specifically in terms of the chemical shift of the β-protons. For example, in the free base form, the b and b′ and e and e′ protons resonate at 18.90 ppm, while the same protons in the protonated form resonate between 7.57−8.62 ppm. Similarly, the c and c′ and f and f′ protons also experience dramatic shielding; in the free base form, it resonates at 13.59 ppm, while in the protonated form, it resonates between 8.03−8.28 ppm. However, the β-protons, d and d′ and a and a′ experience a small shielding after protonation. These observations suggest that these four pyrrole rings are dynamic in nature and change the conformation. A pictorial representation of changes upon protonation is shown in Scheme 1.

Figure 2 shows the temperature-dependent NMR spectra of the free base form of **10**. In this case, the β-pyrrole protons c and c′ resonate at 4.05 and 3.65 ppm, respectively, suggesting a partial inversion of the pyrrole rings. The β-protons of the other two pyrrole rings a and a′ resonate at 19.78 and 21.32 ppm, clearly suggesting no ring inversion. These assignments are based on ^{1}H−^{1}H COSY and HSQC spectrum. The HSQC spectrum of **10** shown in Figure 3 clearly reveals the ^{1}H−^{13}C correlation observed for a and a′, b and b′, and c and c′ protons. The chemical shifts of b and b′ protons at 3.06 and 3.08 ppm also reveal a partial inversion of the two thiophene rings. Upon

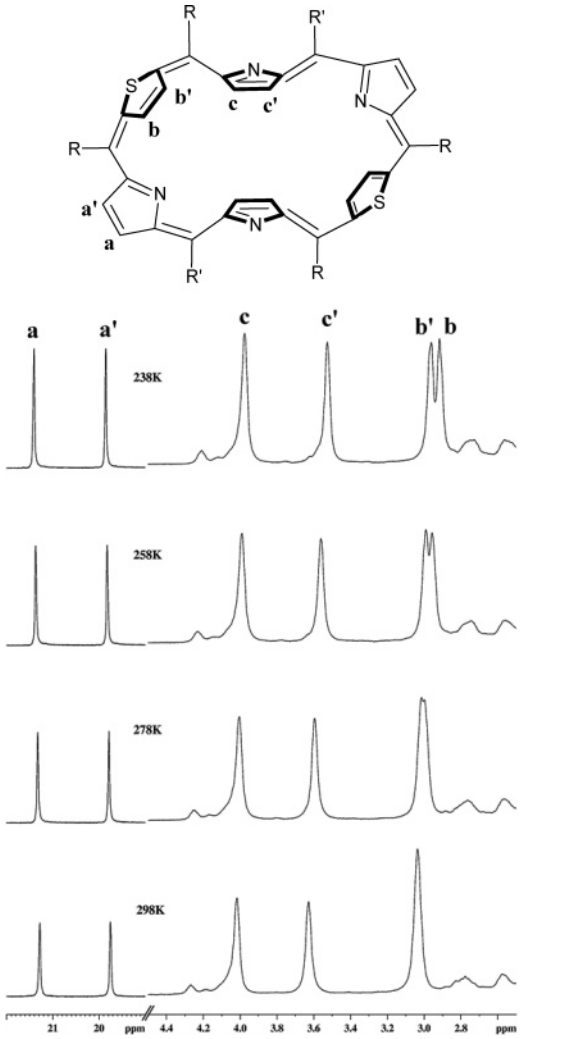


FIGURE 2. Temperature-dependent ^{1}H NMR of **10** in CD_2Cl_2.

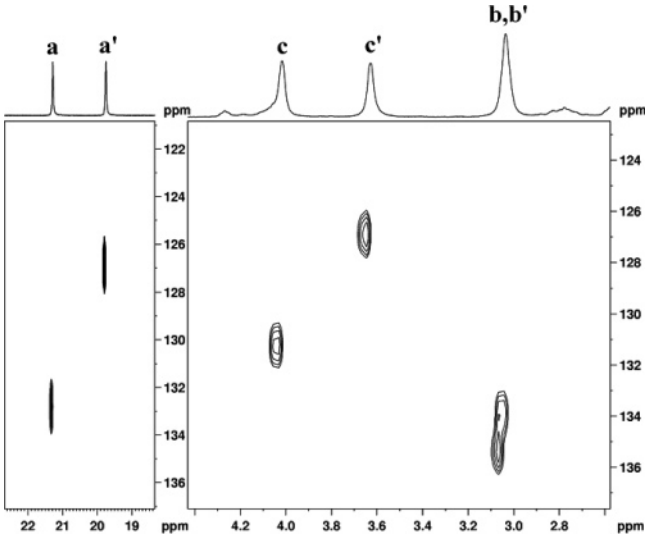
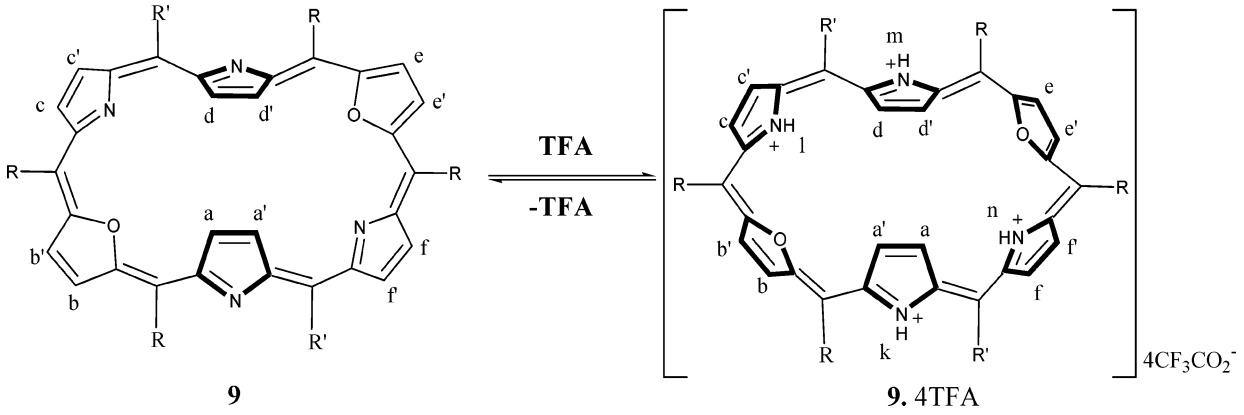


FIGURE 3. HSQC spectrum of **10** at 298 K in CD_2Cl_2.

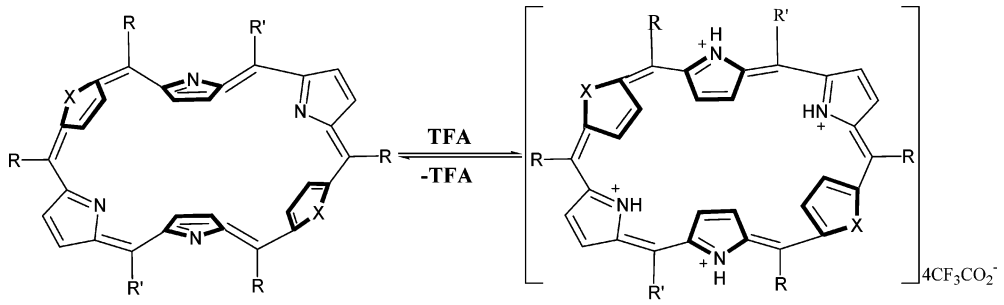
protonation, the c and c′ protons of the center pyrrole rings experience a significant shielding and resonate at 1.6 and 1.4 ppm, and the corresponding NH protons attached to these pyrrole rings resonate at 35.75 ppm, clearly suggesting the

SCHEME 1. Conformational Changes upon Protonation of 9 by TFA



9 **9.** 4TFA

SCHEME 2. Conformational Changes of 10 and 11 upon Protonation by TFA



X = S **10**
X = Se **11**

X = S **10.** 4TFA
X = Se **11.** 4TFA

inversion of these rings (see Supporting Information). On the other hand, β-pyrrole protons of the other two pyrrole rings a and a′ are significantly deshielded and resonate at 28.20 and 27.63 ppm. The corresponding NH protons are observed at 0.98 ppm, suggesting that these two pyrrole rings are not inverted. The β-protons of thiophene rings b and b′ also experience significant shielding in the protonated state and resonate at 0.86 and 0.51 ppm, suggesting the inversion of these rings. The diselenahexaphyrin **11** also shows a similar NMR pattern, suggesting a similar structure.

Thus, the changes occurring in the solution structure of **10** and **11** upon protonation are depicted in Scheme 2. It is interesting to note that in the case of **10** and **11**, four heterocyclic rings are inverted upon protonation, while in the case of **9**, only two pyrrole rings are completely inverted. Interestingly, this structural difference between **9** and **10** was also observed previously in the case of rubyrins.[13]

A comparison of core-modified hexaphyrins reported here with all-aza hexaphyrins reported in the literature reveals some interesting observations. The core-modified hexaphyrins **9**−**11** in the free base form show only partial ring inversion, and the degree of ring inversion depends on the nature of the heteroatom present. However, on protonation, four rings are inverted, and both the forms exhibit aromatic behavior. On the other hand, all-aza hexaphyrins reported by Cavaleiro et al. exhibit a rectangular conformation that consists of two opposite, inverted pyrroles with nitrogen atoms pointing outward and the four corner pyrroles with nitrogen atoms pointing inward. Furthermore, they show both planar and figure eight conformations depending on the nature of the meso substituents and β-substituents.[5,9] In general, hexaphyrins exhibiting a planar structure show aromatic character, while hexaphyrin with a figure eight structure is nonaromatic. Interstingly, all-aza hexaphyrin reported by Anderson et al. that has two different meso substituents (triisopropylsilylacetylenyl and anthryl) does not show aromatic character in spite of its planar structure.[5b] These observations reveal that the subtle changes on the periphery of hexaphyrin can fine-tune the aromatic nature as well as the conformation of the hexaphyrin.

UV−**Vis Spectral Studies.** The electronic absorption spectral studies also reveal conformational changes occurring after protonation. In general, the electronic absorption spectrum of hexaphyrins is characterized by the presence of an intense Soret-like absorption band in the region 500−550 nm and weak Q bands from 550−1000 nm. For example, the free base form of **9** in Figure 4a shows a sharp Soret-like absorption at 546 nm ($\epsilon = 1.95 \times 10^5$) followed by a weak Q band-like absorption in the region 675−1075 nm. Upon protonation, the Soret-like band experiences a 70 nm red shift with an increase in ϵ to 2.42×10^5. There is a clear color change; the free base form is violet, and the tetracationic form is blue. However, in the case of **10** and **11**, the Soret band is split (Figure 4b) with multiple bands in free base form, while in the protonated form, the Soret band experiences a large red shift of 40 and 119 nm, respectively, and the band becomes more intense and sharp. Here also the color changes from violet to blue. The observation of multiple split Soret bands in **10** and **11** relative to the free base form of **9** clearly suggests different degree of ring inversions in the free base of **10** and **11** as reflected in the ^{1}H NMR studies. However, upon protonation, in all the three cases, the Soret-like band is more intense and quite sharp, suggesting a more

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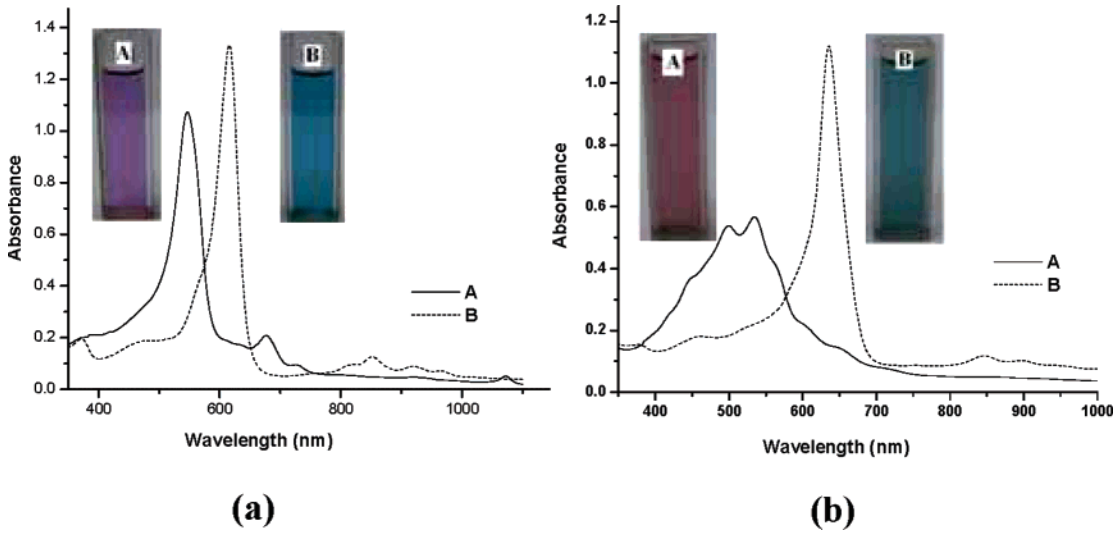

FIGURE 4. Electronic absorption spectra of (a) **9** (5.49×10^{-6} M) and (b) **11** (5×10^{-6} M) in CH_2Cl_2. A and B represent free base and protonated form of corresponding hexaphyrins. The cuvette shows color changes observed after protonation. Protonation was performed by adding a dilute solution of TFA in CH_2Cl_2. The counteranion is $CF_3CO_2^-$.

planar structure as compared to the corresponding free base forms. These absorption spectral changes in the free base and protonated forms taken together suggest a porphyrinic nature of the macrocycle, and the high ϵ value observed for Soret-like absorption supports the aromatic nature of macrocycles.

Conclusion

In this study, we have reported an easy and efficient method for the synthesis of 26π core-modified hexaphyrin using easily available precursors. The advantage of the methodolodgy is the formation of a single product avoiding complex separation problems in addition to the higher yields. The methodology can be applicable to the use of both sterically crowded electron donating aldehydes as well as to electron deficient aldehydes. The isolated hexaphyrins in all cases show aromatic character. The NMR studies reported here clearly support that the ring inversion in hexaphyrins is very sensitive to the state of protonation and that it is dependent on the nature of the heteroatom present in the hexaphyrin. Furthermore, the chemical shifts observed for various protons are used to assess the degree of ring inversion. The protonated form of dioxahexaphyrin **9** shows four partially inverted rings and two completely inverted rings, while the protonated form of dithiahexaphyrin **10** and diselenahexaphyrin **11** shows four completely inverted rings and two planar rings. The clear reversible naked eye color change observed upon protonation allows one to use them for sensor applications. Studies in this direction as well as photophysical properties are underway.

Experimental Section

All NMR solvents were used as received. Solvents like dichloromethane, tetrahydrofuran, and *n*-hexane were purified and distilled by standard procedures. Diols and tripyrranes were synthesized according to published procedures and stored under an inert atmosphere.

Synthesis of Hexaphyrins. (a) Using Trifluoroacetic Acid as Catalyst. 5,10,20,25-Tetramesityl-15,30-dipentafluorophenyl-35-38-dioxahexaphyrin (9). The 5,10-dimesityl-21-oxatripyrrane **7a** (0.5 g, 1.081 mmol) and pentafluorobenzaldehyde **8** (0.133 mL, 1.081 mmol) were dissolved in dry dichloromethane (150 mL) and stirred under nitrogen atmosphere for 10 min. Trifluoroacetic acid (0.041 mL, 0.54 mmol) was added, and the stirring was continued for a further 90 min. Chloranil (0.8 g, 3.24 mmol) was added, and the reaction mixture was exposed to air and refluxed for a further 90 min. The solvent was evaporated in vacuum. The residue was purified by chromatography on a basic alumina column. The pink band that eluted with dichloromethane/petroleum ether (2:3) gave dioxahexaphyrin **9** (0.049 g, 3.56%). ^{1}H NMR (400 MHz, CD_2Cl_2, 238 K, TMS): δ −2.61 (s, 2H), 1.20 (s, 12 H), 1.25 (s, 12 H), 1.31 (s, 12 H), 3.54 (s, 1H), 3.70 (s, 1H), 6.07 (s, 8H), 13.59 (s, 4H), 18.90 (s, 4H); ^{1}H NMR (400 MHz, CD_2Cl_2/TFA, 238 K, TMS): δ −2.87 (d, J = 3.2 Hz, 1H), −3.03 (d, J = 3.6 Hz, 2H), −0.14 (brs, 1H), 0.13 (brs, 1H), 1.21 (s, 12 H), 1.25 (s, 12 H), 1.31 (s, 12 H), 3.54 (d, J = 4.8 Hz, 2H), 4.50 (d, J = 4.8 Hz, 2H), 7.40 (s, 8H), 7.57 (d, J = 4.4 Hz, 2H), 7.75 (brs, 1H), 8.46 (d, J = 4.4 Hz, 2H), 8.62 (s, 2H), 8.28 (d, J = 4.8 Hz, 1H), 8.22 (d, J = 4.4 Hz, 1H), 8.03 (m, 2H), 14.75 (s, 1H). FAB MS: *m*/*z* (%): 1274 (70) [(M + 3)$^+$] UV/vis(CH_2Cl_2): λ_{max}($\epsilon \times 10^{-4}$ M^{-1} cm^{-1}); 546 (19.51), 677 (3.79), 726 (1.73), 920 (0.008), 1072 (0.92); (CH_2Cl_2/TFA): λ_{max} ($\epsilon \times 10^{-4}$ M^{-1} cm^{-1}); 616 (24.24), 851 (2.29), 919 (1.62), 964 (1.29); elemental analysis calcd (%) for $C_{78}H_{56}F_{10}N_4O_2$: C 73.69, H 4.44, N 4.40; found C 73.68, H 4.46, N 4.40. The previous procedure was followed for the synthesis of **10** and **11**.

(b) Using Paratoluenesulphonic Acid (PTSA) as a Catalyst. 5,10,20,25-Tetramesityl-15,30-dipentafluorophenyl-35,38-dithiahexaphyrin (10). The 5,10-dimesityl-21-thiatripyrrane **7b** (0.6 g, 1.25 mmol) and pentaflourobenzaldehyde (0.15 mL,1.25 mmol) were dissolved in dry dichloromethane (200 mL) and stirred under nitrogen atmosphere for 10 min, *p*-toluenesulphonic acid (0.11g, 0.62 mmol) was added, and the stirring was continued for a further 90 min. Chloranil (0.3 g, 1.25 mmol) was added, and the reaction mixture was exposed to air and refluxed for a further 90 min. The solvent was evaporated in vacuum. The residue was purified by chromatography on a basic alumina column. The pink band that eluted with dichloromethane/petroleum ether (3:7) gave 26π dithiahexaphyrin **10** (0.22 g, 16%). ^{1}H NMR (400 MHz, CD_2Cl_2, 238 K, TMS): δ 1.26 (s, 12 H), 1.29 (s, 12 H), 1.34 (s, 12 H), 3.06 (s, 2H), 3.08 (s, 2H), 3.65 (s, 2H), 4.05 (s, 2H), 7.40 (s, 8H), 19.78 (s, 2H), 21.32 (s, 2H); ^{1}H NMR (400 MHz, CD_2Cl_2/TFA, 218 K, TMS): δ 0.51 (s, 2H), 0.86 (s, 2H), 0.98 (brs, 2H), 1.24 (s, 12 H), 1.25 (s, 12 H), 1.32 (s, 12 H), 1.4 (s, 2H), 1.6 (s, 2H), 7.37 (s, 8H), 27.63 (s, 2H), 28.20(s, 2H), 35.75 (brs, 2H). FAB MS: *m*/*z* (%): 1306 (100) [(M + 3)$^+$]; elemental analysis calcd (%) for

$C_{78}H_{56}F_{10}N_4S_2$: C 71.87, H 4.33, N 4.29; found C 71.88, H 4.34, N 4.30; UV/vis (CH_2Cl_2): λ_{max} ($\epsilon \times 10^{-4}$ M^{-1} cm^{-1}); 500 (1.91), 538 (2.27), 569 (2.22): (CH_2Cl_2/TFA): λ_{max} ($\epsilon \times 10^{-4}$ M^{-1} cm^{-1}); 593 (3.12), 804 (0.39). The previous procedure was followed for the synthesis of **11**.

(c) Using DDQ as the Oxidant. 5,10,20,25-Tetramesityl-15-30-dipentafluorophenyl-35,38-diselenahexaphyrin (11). The 5-10-dimesityl-21-selenatripyrrane **7c** (0.4 g, 0.76 mmol) was dissolved in dry CH_2Cl_2 (5 mL) and stirred under nitrogen for 10 min. Pentafluorobenzaldehyde **8** (0.094 mL, 0.76 mmol) in 2 mL of CH_2Cl_2 was added, and the stirring continued for a further 2 h. Dichlorodicyanoquinone (DDQ) (0.17 g, 0.76 mmol) in 2 mL of dry toluene was added and stirred for an additional 2 h. The solvent was evaporated under reduced pressure, and the residue was subjected to chromatographic purification on basic alumina. A pink fraction eluting with 1:1 [hexane/CH_2Cl_2] gave a dark green solid identified as the title compound. Yield: 0.081 g, 7.6%. ^{1}H NMR (400 MHz, CD_2Cl_2/TFA, 218 K, TMS): δ −1.21 (brs, 2 H), −1.08 (s, 4H), 0.15 (s, 2H), 0.21 (s, 2H), 1.27 (s, 12 H), 1.96 (s, 12 H), 2.12 (s, 12 H), 5.48(s, 4H), 5.64 (s, 4H), 31.87 (s, 2H), 31.94 (s, 2H), 40.45 (brs, 2H); FAB MS: *m*/*z* (%): 1400 (100) [(M + 3)$^+$]; elemental analysis calcd (%) for $C_{78}H_{56}F_{10}N_4Se_2$: C 67.05, H 4.04, N 4.01; found C 67.06, H 4.05, N 4.00. UV/vis (CH_2Cl_2): λ_{max} ($\epsilon \times 10^{-4}$ M^{-1} cm^{-1}); 499 (10.77), 534 (11.3) (CH_2Cl_2/TFA): λ_{max} ($\epsilon \times 10^{-4}$ M^{-1} cm^{-1}); 635 (22.51), 847 (2.48), 898 (2.18). The previous procedure was followed for the synthesis of **10**.

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Supporting Information Available: HSQC and 2-D COSY spectra of compound **9**, titration studies of free base of **10** with TFA at variable temperatures, and HSQC spectrum of the protonated form of **10** at 238 K. This material is available free of charge via the Internet at http://pubs.acs.org.

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