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ansa-Ferrocene-Incorporated Calixpyrroles and Calixphyrins: Syntheses and Spectral/Structural Characterization

S. Ramakrishnan,[†] K. S. Anju,[†] Ajesh P. Thomas,[‡] K. C. Gowri Sreedevi,[†] P. S. Salini,[†] M. G. Derry Holaday,[†] Eringathodi Suresh,[§] and A. Srinivasan*[,‡]

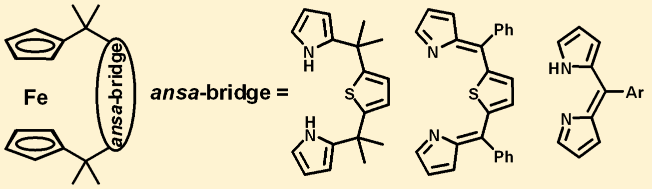
[†]Photosciences and Photonics Section, Chemical Sciences and Technology Division, National Institute for Interdisciplinary Science and Technology (NIIST−CSIR), Thiruvananthapuram−695019, Kerala, India

[‡]School of Chemical Sciences, National Institute of Science Education and Research (NISER), Bhubaneswar−751005, Odisha, India

[§]Analytical Science Discipline, Central Salt and Marine Chemical Research Institute (CSMCRI-CSIR), G. B. Marg, Bhavnagar−364002, Gujarat, India

Supporting Information

ABSTRACT: The syntheses and spectral/structural characterization of *ansa*-ferrocene-incorporated *normal* calixphyrins and *core-modified* calixpyrroles and calixphyrins are reported. Acid-promoted dehydrative condensation of 1,1′-bis(dimethylpyrrolylmethyl)ferrocene and 2,5-bis(dimethylhydroxymethyl)thiophene/furan yielded *ansa*-ferrocene-based *core-modified* calixpyrroles, while acid-catalyzed dehydrative condensation of 1,1′-bis(diphenylpyrrolylmethyl)ferrocene with the aryl aldehydes and 2,5-bis(phenylhydroxymethyl)thiophene followed by DDQ oxidation resulted in the formation of *ansa*-ferrocene-appended *normal* and *core-modified* calixphyrins, respectively. The newly synthesized macrocycles were characterized by FAB-MS, NMR, and UV−vis spectral analyses and finally confirmed by single-crystal X-ray structural analysis. All these studies clearly revealed the introduction of ferrocene in the main framework of the corresponding macrocycles in an *ansa*-type way. The *core-modified* calixpyrroles adopt a 1,3-alternate conformation, while the corresponding calixphyrins maintained partial planarity along the tripyrrin plane due to the presence of *meso* sp^2 carbon and generated curved staircase conformation. In addition to the intramolecular hydrogen-bonding interactions, calixphyrins generate self-assembled dimers, one- and two-dimensional supramolecular assemblies through intermolecular hydrogen bonding in the solid state.



■ INTRODUCTION

Porphyrinogens, the *meso*-reduced derivatives of porphyrins, have significant roles in both natural and artificial systems.[1] Their rich anion binding abilities, metal complexation character, unique redox properties, molecular recognition behavior, etc., make them versatile molecules.[1] Introduction of dialkyl or diaryl or alkyl-aryl substituents onto the *meso* sp^3-hybridized carbon prevents the oxidative aromatization of porphyrinogens to porphyrins. However, the important difference lies in the coordination behavior of porphyrins and porphyrinogens; the former are dianionic ligands, whereas the latter are tetra-anionic ligands toward metal complexation.[1] There are two types of porphyrinogens: calixpyrroles,[1e] where all the *meso* carbons are sp^3 hybridized, and calixphyrins,[1d,f,g] where at least one of the *meso* carbons is sp^2 hybridized. A series of calixpyrroles, namely, calix[5]pyrrole,[2,4] calix[6]pyrrole,[3] hexadecafluorocalix[8]pyrrole,[4] calixbipyrrole,[5] strapped calixpyrrole,[6] calixpyrrole dimer,[7] N-confused calix[4]pyrrole,[8] cryptand-like calixpyrrole,[9] aza tri- and tetrapyrrolic macrocycles,[10] calix[1]pyrene[3]pyrrole,[11] *expanded* calix[*n*]pyrrole,[12] and *core-modified* calixpyrroles having benzene,[13] carbazole,[14] furan,[5b,15] phosphole,[16] and thiophene[5b,15a,c,e,17] analogues, are reported. Many examples of calixphyrin derivatives, such as phlorins,[18] isoporphyrins,[19] 5,10- or 5,15-dihydroporphyrins,[18f,20] porphomono,[21] and dimethenes,[20,21a,b,22] higher order calix[*n*]phyrins ($n > 4$),[1d,23] three-dimensional calixphyrin,[24] hybrid calixphyrins,[22e−i,25] and N-confused calixphyrins[26] are known in the literature.

On the other hand, the metallocenes have been used as electrochemically active substituents, which are covalently or noncovalently linked to the receptor moieties such as porphyrinogens and single- or multi-porphyrin assemblies. In 1998, Sessler and co-workers reported an *ansa*-ferrocene-bridged macrocycle (**A**) (Chart 1) in which the ferrocene subunit is covalently bonded with two pyrrole units strapped with an amide-linked oligoether, which acts as a redox-based sensor for F$^-$ and H$_2$PO$_4^-$ anions.[27] In 2001, another group reported a *meso* ferrocenyl calix[4]pyrrole (**B**) (Chart 1) where the ferrocene is substituted at one of the *meso* positions of the calixpyrrole framework, which has been tested as an electrochemical sensor for various anions.[28f] Recently, Bucher and co-workers reported *meso* ferrocenyl calix[4]phyrin (**C**) (Chart 1), which contains only one sp^2-hybridized *meso* carbon with a

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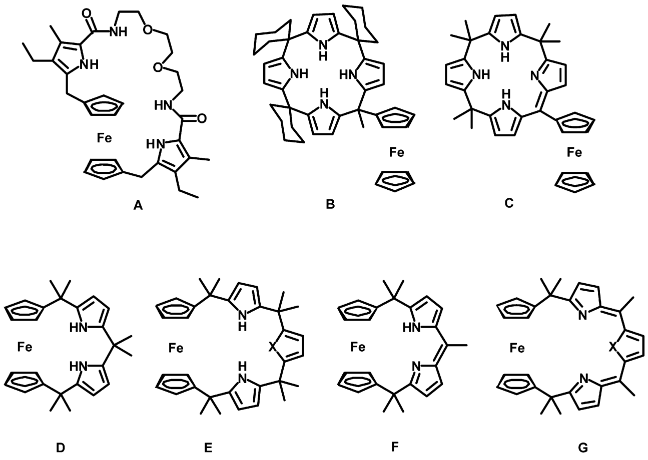
Chart 1

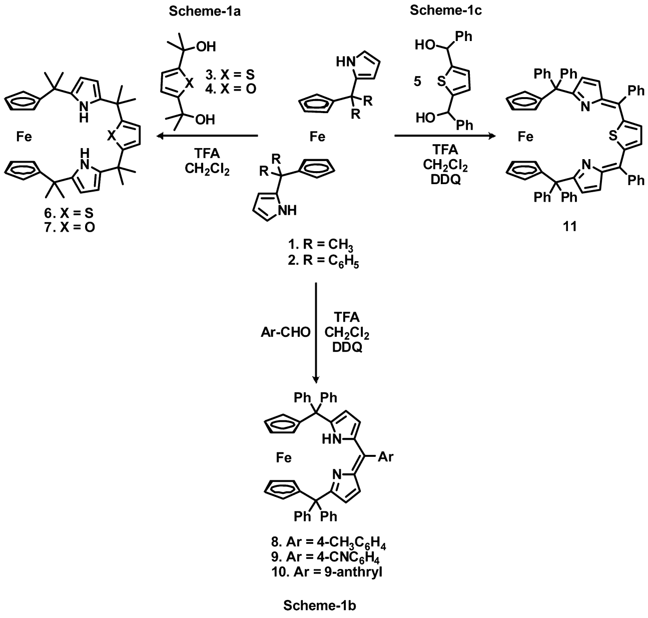


ferrocene unit.[28g] In addition to these, metallocene-appended porphyrins[28a−e] have also been synthesized, which were found suitable for multiple electron transfer reactions and molecular electronic devices.[27,28] However, incorporation of metallocenes into the integral part of the fully/partially conjugated macrocycles is rare.[27,29]

Recently, we have demonstrated the syntheses and spectral/structural characterization of *normal* calix[1]metallocenyl[2]-pyrrole (**D**)[29a] (Chart 1), where the pyrrole units in the main framework adopt a 1,2-alternate conformation in the solid state, proving that the macrocycle retains the calix[4]pyrrole behavior.[1e] Subsequently, Latos-Grażyński and co-workers reported *ansa*-metallocene macrocycles in which the metallocene is connected with a conjugated oligopyrrole unit, such as dipyrrin (**F**) or heterotripyrrin (**G**), where the helical conformations and dynamic behavior of these macrocycles have been explored by NMR spectroscopy.[29b] Very recently, the same group also reported the synthesis and characterization of ferrocenothiaporphyrin and dihydroferrocenothiaporphyrin, which possessed macrocyclic antiaromaticity and aromaticity and provided evidence for direct transmission of π-electron conjugation across a d-electron metallocene.[29c] In addition to the metallocene-appended dipyrrin macrocycle (**F**)[29b] (Chart 1) reported by Latos-Grażyński et al., very recently, we synthesized *expanded* calix[n]metallocenyl[m]phyrins,[29d] where the macrocycles bear analogy to both calixpyrrole and porphyrin macrocycles, generating a two-dimensional supramolecular assembly in the solid state, and the role of aryl versus alkyl in the *meso* position of 1,1′-ferrocenyldipyrromethane was also highlighted to explain the formation of *expanded* macrocycles. In all these macrocycles, metallocene units are incorporated into the backbone of the respective macrocyclic framework. Introduction of one more heterocyclic rings such as thiophene/furan in the above-mentioned metallocene-appended porphyrinogen framework leads to novel *expanded* macrocycles having unusual spectral properties due to altered electronic structure and core sizes. Herein, we wish to report the syntheses and spectral/structural characterization of *ansa*-ferrocene-incorporated *core-modified* calixpyrrole (**E**) and *normal* (**F**) and *core-modified* calixphyrin (**G**)[29b] (Chart 1).

■ RESULTS AND DISCUSSION

Scheme 1. Syntheses of 6−11



Syntheses. The syntheses of *ansa*-ferrocene-incorporated *core-modified* calixpyrroles and *normal* and *core-modified* calixphyrins are summarized in Scheme 1. Scheme 1a utilizes trifluoroacetic acid-catalyzed condensation reaction of **1**[29a] with **3** and **4**[30] in CH_2Cl_2 followed by column chromatographic purification, resulting in stable yellow-colored macrocycles **6** and **7** in 28% and 27% yield, respectively, whereas Scheme 1b and c involved similar acid-catalyzed condensation of **2** with equimolar quantity of aryl aldehydes and **5**[31] followed by oxidation with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ), resulting in the formation of stable red-colored macrocycles **8**−**10** in 17−19% and **11** in 4% yield.[29e] However, no higher analogues could be isolated upon purification of the crude mixture. All the macrocycles are soluble in almost all the organic solvents such as CH_2Cl_2, $CHCl_3$, and CH_3CN.

Spectral Analyses. The FAB mass spectral analyses of all the new macrocycles **6**−**11** show the molecular ion signals at 564.87, 548.60, 748.22, 758.80, 834.08, and 904.68, respectively, which proves the exact composition. The ^{1}H NMR spectra of **6**−**11** (Table 1) were recorded in $CDCl_3$ at room temperature (Figure 1), where the NH protons of the macrocycles **6** and **7** appeared as a broad singlet with a chemical shift value of 8.21 and 8.36 ppm, respectively. Incorporation of one more heterocyclic ring in the macrocycles (**6** and **7**) leads to 0.33 and 0.48 ppm downfield shifts of the NH protons as compared to *normal* calix[1]ferrocenyl[2]-pyrrole (**D**),[29a] suggesting expansion in the macrocyclic framework.

Table 1. NMR Spectral Data of 6−11

compound	NH (ppm)	β-pyrrolyl, β-[a]thienyl/[b]furanyl CH (ppm)	ferrocenyl CH (ppm)
6	8.21	5.98−5.96, 5.87−5.85, [a]6.78	4.19−3.97, 3.35
7	8.36	5.96−5.95, [b]6.05	4.02−3.82
8	16.26	6.62−6.61, 5.81−5.8	4.59, 3.94, 3.86, 2.89
9	16.18	6.48−6.47, 5.87−5.85	4.57, 3.97, 3.86, 2.93
10	16.41	5.98−5.97, 5.69−5.67	4.76, 4.01, 3.90, 3.02
11		6.78−6.77, 6.64−6.63, [a]6.74	5.86, 4.14, 3.66, 3.01

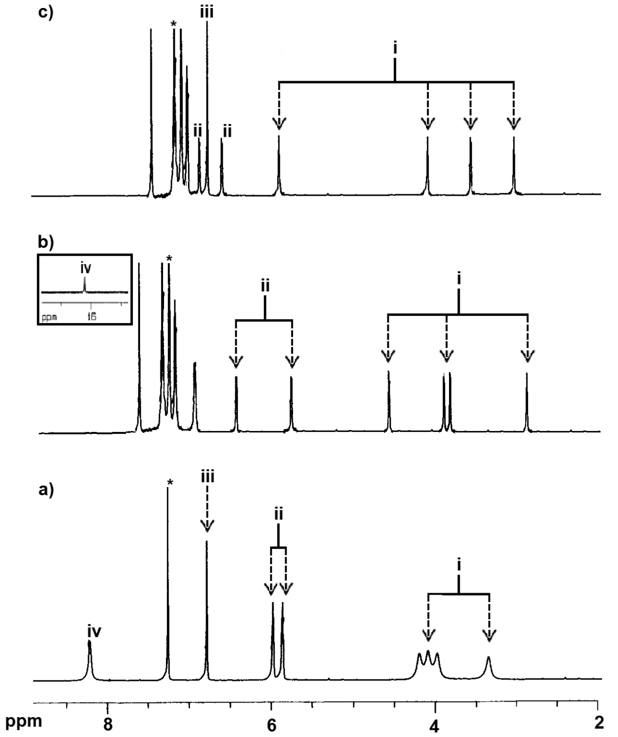


Figure 1. ^1H NMR spectra of (a) **6**, (b) **9**, and (c) **11** in $CDCl_3$. (i) Ferrocenyl CH, (ii) pyrrolic-β-CH, (iii) thienyl-β-CH, (iv) NH. *Solvent peak, and the remaining are phenyl protons.

The NH protons of the macrocycles **8**–**10** appeared as a broad singlet at the high deshielded region with a chemical shift value of 16.26, 16.18, and 16.41 ppm, respectively. The drastic shift of NH is mainly due to delocalization of the lone pair of electrons on the pyrrolyl amine nitrogen atom of the macrocycles and also the presence of an intramolecular hydrogen-bonding interaction between amine NH and imine N in the dipyrrin moiety. All the NH protons of **6**–**10** were confirmed by D_2O exchange experiments.

The thienyl-β-CH protons of **6** and **11** appeared as a singlet at 6.78 and 6.74 ppm, whereas furanyl-β-CH protons of **7** appeared at 6.05 ppm. Due to the heavier heteroatom effect, the thienyl-β-CH protons in **6** are 0.73 ppm deshielded when compared with the furanyl-β-CH protons of **7**. The pyrrolic-β-CH protons of all the macrocycles **6**–**11** resonated between 6.8 and 5.6 ppm. Due to partial delocalization of electron density, the pyrrolic-β-CH protons of **11** are deshielded with a shift difference of 0.80 ppm when compared with **6**. The disappearance of the pyrrolic-α-CH proton peaks of **1** at 6.48 ppm and **2**[29a] at 6.69 ppm suggests the formation of macrocycles **6**–**11**.

Finally, the ferrocenyl CH protons of **6** and **7** split into two different sets to give a multiplet resonating at 4.19–3.80 ppm and a singlet at 3.35 ppm. However, in **11**, out of eight protons, two protons appeared as a singlet at the deshielded region with a shift value of 5.86 ppm, whereas the remaining six protons resonated between 4.14 and 3.01 ppm. In the case of **8**–**10**, the respective protons resonated as a set of four singlets between 4.76 and 2.89 ppm. This suggests that two cyclopentadienyl rings in **8**–**11** are in restricted rotation at room temperature due to the presence of four phenyl rings on two sp^3-hybridized *meso* carbons which are directly attached to the 1 and 1′ position of ferrocene.

Ultraviolet–Visible Spectral Analyses. The UV–vis spectral characteristics of the macrocycles **8**–**11** (Table 2) turned out to be generally comparable to those of calix[*n*]-phyrin-type macrocycles.[29d] In the electronic spectral analysis of the macrocycles **8**–**11** in $CHCl_3$, broad absorption bands, which originated due to $\pi \rightarrow \pi^*$ transitions in the dipyrrin moiety, were observed between 400 and 575 nm with molar extinction coefficient values ranging from 33 000 to 1 90 000 $M^{-1}cm^{-1}$. Absorption spectra of **11** were red-shifted by 20–25 nm compared with **8**–**10**, which proves the extended π-conjugation in **11** (Figure 2). The absorption bands corresponding to $\pi \rightarrow \pi^*$ transitions of the anthracene moiety were observed at the lower wavelength absorption region between 332 and 386 nm with molar extinction coefficient values ranging from 96 000 to 49 000 M^{-1} cm^{-1}, respectively for **10** (Figure 2). All the macrocycles are nonfluorescent in their free base form.

Table 2. Absorption Spectral Data of 8–11

compound in $CHCl_3$	λ_{abs} ($\varepsilon \times 10^5$) [nm (M^{-1} cm^{-1})]
8	468.5 (0.33)
9	467.4 (0.38)
10	332 (0.497), 348.5 (0.71), 366.5 (0.957), 386 (0.94), 474.5 (1.9)
11	494.8 (0.38), 520 (0.41)

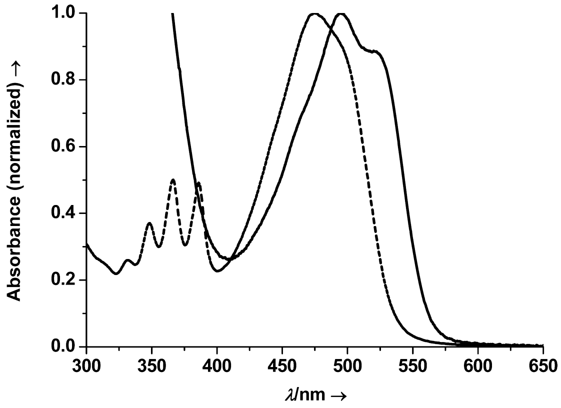


Figure 2. UV–vis absorption spectra of **10** (dotted line) and **11** (solid line) in $CHCl_3$.

Single-Crystal X-ray Structural Analyses. The final confirmation of the macrocycles **6** and **8**–**11** comes from single-crystal X-ray structural analyses (Table 3), which are shown in Figures 3, 4, and 5. Good-quality X-ray crystals of **6** and **8**–**11** were grown by slow diffusion of heptanes into their $CHCl_3$ solutions. As predicted from the above observations, one ferrocene, two pyrrole units, and two *meso* sp^3-hybridized carbons each containing two methyl groups in **6** and two phenyl groups in **8**–**11** are present, where the α position of the pyrrole groups is connected to the 1 and 1′ position of ferrocene via sp^3-hybridized *meso* carbon bridges. On the other hand, the α' position of the pyrrole units is connected with thiophene through two sp^3 *meso* carbons containing four methyl groups in **6** and two sp^2 *meso*-carbons containing two phenyl groups in **11** to form the *core-modified expanded* calixpyrrole and calixphyrin, whereas with various aryl moieties

Table 3. Crystal Data, Data Collection and Refinement Parameters for Compounds 6 and 8–11

parameter	6	8	9	10	11
empirical formula	$C_{34}H_{40}FeN_2S$	$C_{52}H_{40}FeN_2$	$C_{52}H_{37}FeN_3$	$C_{59}H_{41}FeN_2$	$C_{63}H_{47}Cl_3FeN_2S$
M_w	564.59	748.71	759.70	833.79	1026.29
T [K]	293(2)	100(2)	100(2)	100(2)	100(2)
λ [Å]	0.71073	0.71073	0.71073	0.71073	0.71073
cryst syst	monoclinic	monoclinic	monoclinic	triclinic	triclinic
space group	Cc	$P2_1/n$	$P2_1/c$	$P\bar{1}$	$P\bar{1}$
a [Å]	10.8142(6)	16.4365(15)	18.3257(17)	10.7256(16)	10.8554(14)
b [Å]	22.5198(14)	9.8425(9)	15.9064(15)	13.681(2)	13.2066(17)
c [Å]	13.0638(7)	23.296(2)	12.7614(11)	17.613(2)	17.776(2)
α [deg]	90.00	90.00	90.00	112.668(2)	99.425(2)
β [deg]	113.378(3)	91.443(2)	93.401(2)	93.344(3)	101.517(2)
γ [deg]	90.00	90.00	90.00	105.922(2)	94.053(2)
V [Å^3]	2920.3(3)	3767.5(6)	3713.3(6)	2253.8(5)	2449.3(5)
Z, ρ_{calcd} [Mg m^{-3}]	4, 1.284	4, 1.320	4, 1.359	2, 1.229	2, 1.389
μ(Mo Kα) [mm^{-1}]	0.613	0.441	0.449	0.376	0.559
cryst size [mm]	0.30 × 0.20 × 0.20	0.42 × 0.32 × 0.19	0.40 × 0.24 × 0.14	0.35 × 0.20 × 0.15	0.32 × 0.21 × 0.11
θ range for data collection [deg]	1.81 to 30.99	1.50 to 28.26	1.70 to 25.00	1.65 to 25.00	1.19 to 28.27
limiting indices	$-15 \leq h \leq 15$, $-32 \leq k \leq 32$, $-18 \leq l \leq 17$	$-21 \leq h \leq 21$, $-12 \leq k \leq 13$, $-30 \leq l \leq 30$	$-21 \leq h \leq 16$, $-18 \leq k \leq 18$, $-11 \leq l \leq 15$	$-12 \leq h \leq 12$, $-16 \leq k \leq 15$, $-20 \leq l \leq 20$	$-14 \leq h \leq 14$, $-17 \leq k \leq 17$, $-23 \leq l \leq 23$
reflns collected	37 453	31 454	18 392	16 106	21 017
indep reflns [R(int)]	8676 [0.0376]	8910 [0.0613]	6524 [0.0727]	7866 [0.0518]	11 082 [0.0232]
refinement method	full-matrix least-squares on F^2	full-matrix least-squares on F^2	full-matrix least-squares on F^2	full-matrix least-squares on F^2	full-matrix least-squares on F^2
data/restraints/params	8676/4/359	8910/0/501	6524/0/505	7866/0/560	11 082/0/631
goodness-of-fit on F^2	1.007	1.129	1.131	1.043	1.119
final R indices [$I > 2\sigma(I)$]	R1 = 0.0320, wR2 = 0.0849	R1 = 0.0642, wR2 = 0.1305	R1 = 0.0694, wR2 = 0.1286	R1 = 0.0715, wR2 = 0.1830	R1 = 0.0608, wR2 = 0.1450
R indices (all data)	R1 = 0.0400, wR2 = 0.0936	R1 = 0.0841, wR2 = 0.1383	R1 = 0.0942, wR2 = 0.1379	R1 = 0.0960, wR2 = 0.1944	R1 = 0.0673, wR2 = 0.1491
largest $\Delta\rho$ [e Å^{-3}]	0.335 and −0.214	0.588 and −0.545	0.612 and −0.447	0.700 and −0.604	0.796 and −0.519

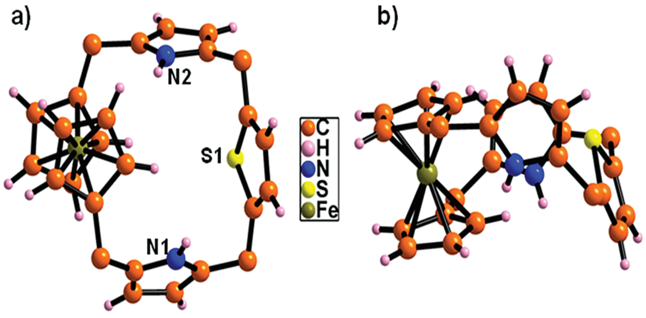


Figure 3. Single-crystal X-ray structure of **6**. (a) Top view, (b) side view. *meso*-Methyl groups are omitted for clarity.

via a sp^2-hybridized *meso* carbon in **8–10** to generate *normal* calixphyrins.

The crystal analysis of **6** shows that both the pyrrole units are arranged in a head-on manner and adopt a 1,3-alternate conformation (Figure 3a) in the solid state, as in the case of the parent calix[4]pyrrole unit,[1e] where the distance between two pyrrolic nitrogens is 5.61 Å.

As observed in the NMR spectral analyses of **11**, the crystal structure also reveals the partial planarity along the tripyrrin plane and adopts a curved staircase like conformation, as shown in Figure 4b. The close observation of **11** shows the formation of three self-assembled dimers through the intermolecular hydrogen-bonding interactions: (a) the phenyl C–H group that is present in the *meso* sp^2 carbon interacts with the thienyl π-cloud; (b) the ferrocenyl C–H moiety interacts with the phenylic π-cloud; and (c) one of the phenylic C–H from the *meso* sp^3 carbon interacts with the ferrocenyl π-cloud. The distances and angles are (a) C40–H40···thiophene (π): 2.74 Å, 156°; (b) C4–H4···phenyl (π): 2.99 Å, 130°; and (c) C35–H35···ferrocenyl (π): 2.96 Å, 143°, respectively. These self-assembled dimers interact with each other to form three one-dimensional arrays (see the Supporting Information), which further combine to generate a two-dimensional supramolecular assembly in the solid state as shown in Figure 4c.

The macrocycles **8–10** are isostructural with earlier reported calix[1]metallocenyl[2]phyrins.[29d] As revealed from the NMR analysis of **8–10**, the amine and imine units in the dipyrrin moiety form intramolecular hydrogen-bonding interactions with bond distances and angles for N2–H2C···N1 in **8**, N1–H1C···N2 in **9**, and N1–H1C···N2 in **10** of 1.89 Å, 137°; 2.03 Å, 122°; and 2.00 Å, 129°, respectively. The *meso-p*-tolyl in **8**, *meso-p*-cyanophenyl in **9**, and *meso*-9-anthryl in **10** are deviated from the mean dipyrrin plane with deviations of 37.76°, 50.52°, and 63.14°, respectively. In addition to intramolecular hydrogen-bonding interactions, **8** also generates a self-assembled dimer and one-dimensional array (Figure 5g) through the intermolecular hydrogen-bonding interactions. One of the *meso*-phenyl C–H units (C51–H51) in **8** interacts with the pyrrolic π-cloud to generate a self-assembled dimer, while the *meso*-tolyl C–H unit (C40–H40C) interacts with the *meso*-phenylic π-cloud to form a one-dimensional array, where the

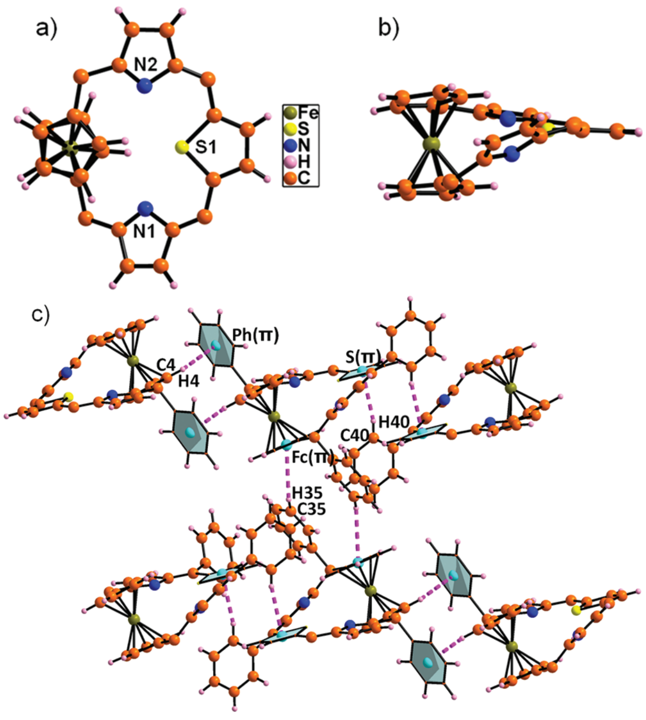


Figure 4. Single-crystal X-ray structure of **11**. (a) Top view, (b) side view, (c) two-dimensional array. *meso*-Phenyl groups and the groups that are not involved in the intermolecular hydrogen-bonding interactions are omitted for clarity.

distances and angles are 2.56 Å, 161° and 2.79 Å, 124°, respectively.

As observed in the case of **11**, **9** also forms three self-assembled dimers through intermolecular hydrogen-bonding interaction, namely, (a) between the *meso*-*p*-cyano benzene units; (b) one of the phenyl C−H units from the *meso* sp^3 carbon with the *meso*-*p*-cyano benzene π-cloud; and (c) the ferrocenyl C−H with one of the *meso*-phenyl unit's π-cloud. The distances and angles are (a) C38−H38···N3: 2.56 Å, 148°; (b) C50−H50···phenyl (π): 2.61 Å, 161°; and (c) C9−H9···phenyl (π): 2.62 Å, 142°, where the self-assembled dimers interact with each other to form a one-dimensional array (see the Supporting Information). Further, combining such dimers and the one-dimensional array, **9** generates a two-dimensional supramolecular assembly in the solid state, which is shown in Figure 5h. On the other hand, in **10**, the β-CH protons of the pyrrolic units (C14−H14 and C18−H18) that are present in the dipyrrin moiety interact with one of the *meso*-phenyl unit's π-cloud through intermolecular hydrogen-bonding interactions to form the one-dimensional array (Figure 5i). The distances and angles are 2.85 Å, 152° and 2.48 Å, 149°, respectively.

CONCLUSION

In summary, the synthetic protocol developed for *ansa*-ferrocene-incorporated *normal* calixphyrins and *core-modified* calixpyrroles and calixphyrins is straightforward due to the absence of side products and easier purification. To the best of our knowledge, this is the first report on *ansa*-ferrocene-based *core-modified* calixpyrrole systems. The present work demonstrates the incorporation of both ferrocene and thiophene/furan simultaneously in the main framework of calixpyrroles and calixphyrins. UV−vis absorption studies show the bands due to dipyrrin and tripyrrin moieties. The structures of these macrocycles have been elucidated by single-crystal X-ray studies. From the structural analyses, *ansa*-ferrocene-based calix[1]thienyl[2]pyrrole adopts a 1,3-alternate conformation and retains the parent calix[4]pyrrole behavior, whereas *ansa*-ferrocene-based calix[2]phyrins and calix[1]thienyl[2]phyrin are partially planar systems and generate curved staircase conformations. In addition to the intramolecular hydrogen-bonding interactions in the dipyrrin moieties, the calixphyrins reported here also generate a series of supramolecular assemblies through intermolecular hydrogen bonding. Due to the presence of ferrocene in an *ansa*-type way, these macrocycles are highly rigid in the solid state. Efforts are currently under way to explore the receptor properties of these macrocycles in our lab.

EXPERIMENTAL SECTION

General Procedures. The starting materials were purchased from S. D. Fine Chemical and Aldrich Chemical Co. and used without further purification unless otherwise stated. All the solvents were purified and distilled before use. Petroleum ether used was the fraction with bp 60−80 °C. NMR spectra were recorded with a Bruker 300 or 500 MHz spectrometer with $CDCl_3$ as solvent. Chemical shifts are expressed in parts per million (ppm) relative to TMS. FAB mass spectra were obtained on a JEOL SX-120/DA6000 spectrometer using argon (6 kV, 10 mA) as the FAB gas. UV/vis spectra were recorded on a Perkin-Elmer−Lambda 25 UV−visible spectrophotometer. TLC analyses were carried out on aluminum sheets coated with silica gel 60 (Merck 5554). Column chromatography was performed on silica gel 100−200 mesh. Cyclic voltammetric studies were done on a CHI model 620B CV apparatus (CH instruments, Inc.) interfaced to a computer. A three-electrode system consisting of a platinum working electrode and commercially available saturated calomel electrodes, a reference electrode, and a platinum mesh counter electrode was used. The reference electrode was separated from the bulk of the solution by a fritted glass bridge filled with the solvent/supporting electrolyte mixture. Half-wave potentials were measured as the average of anodic and cathodic peak potentials.

*Synthesis of **6**.* To a 250 mL flask containing **1** (0.2 g, 0.5 mmol) and **3** (0.1 g, 0.5 mmol) was added 60 mL of dry CH_2Cl_2, and the mixture was allowed to stir for 10 min at room temperature under a N_2 atm. Then TFA (0.01 mL, 0.1 mmol) was added, and the mixture allowed to stir for 45 min. After removal of the solvent, the crude product was purified by silica gel column chromatography, 100−200 mesh. The first moving fraction eluted with EtOAc/petroleum ether (3:97) was identified as yellow solid **6** in 28% yield. Spectral data for **6**: mp >250 °C; ^1H NMR (300 MHz, $CDCl_3$, 298 K, TMS) δ 8.21 (brs, 2H; NH), 6.78 (s, 2H; thienyl-β-CH), 5.98−5.96 (m, 2H; pyrrolic-β-CH), 5.87−5.85 (m, 2H; pyrrolic-β-CH), 4.19−3.97 (m, 6H; ferrocenyl CH), 3.35 (s, 2H; ferrocenyl CH), 1.73 (s, 12H; CH_3), 1.62 (s, 6H; CH_3), 1.26 (s, 6H; CH_3); FAB-MS (*m*/*z*) calcd for $C_{34}H_{40}FeN_2S$ 564.22, obsd 564.87 (100%, M^+). Anal. Calcd (%) for $C_{34}H_{40}FeN_2S$: C 72.33, H 7.14, N 4.96. Found: C 71.25, H 7.17, N 4.87.

*Synthesis of **7**.* The above procedure was followed by using **4** (0.092 g, 0.5 mmol). The first fraction eluted with EtOAc/petroleum ether (3:97) was identified as yellow solid **7** in 27% yield. Spectral data for 7: mp >250 °C; ^1H NMR (300 MHz, $CDCl_3$, 298 K, TMS) δ 8.36 (brs, 2H; NH), 6.05 (s, 2H; furanyl-β-CH), 5.96−5.95 (d, *J* = 2.7 Hz, 4H; pyrrolic-β-CH), 4.02−3.82 (m, 8H; ferrocenyl CH), 2.15 (s, 6H; CH_3), 1.65 (s, 18H; CH_3); FAB-MS (*m*/*z*) calcd for $C_{34}H_{40}FeN_2O$ 548.25, obsd 548.60 (100%, M^+). Anal. Calcd (%) for $C_{34}H_{40}FeN_2O$: C 74.45, H 7.35, N 5.11. Found: C 74.67, H 7.29, N 5.17.

*Synthesis of **8**.* To a 250 mL flask containing **2** (0.2 g, 0.3 mmol) and *p*-tolualdehyde (0.036 mL, 0.3 mmol) was added 100 mL of dry CH_2Cl_2 under inert conditions, and the mixture was allowed to stir for 10 min at room temperature. TFA (0.0007 mL, 0.01 mmol) was added to the above reaction mixture, and the solution allowed to stir for 2 h. To the reaction mixture, 2,3-dichloro-5,6-dicyano-1,4-benzoquinone

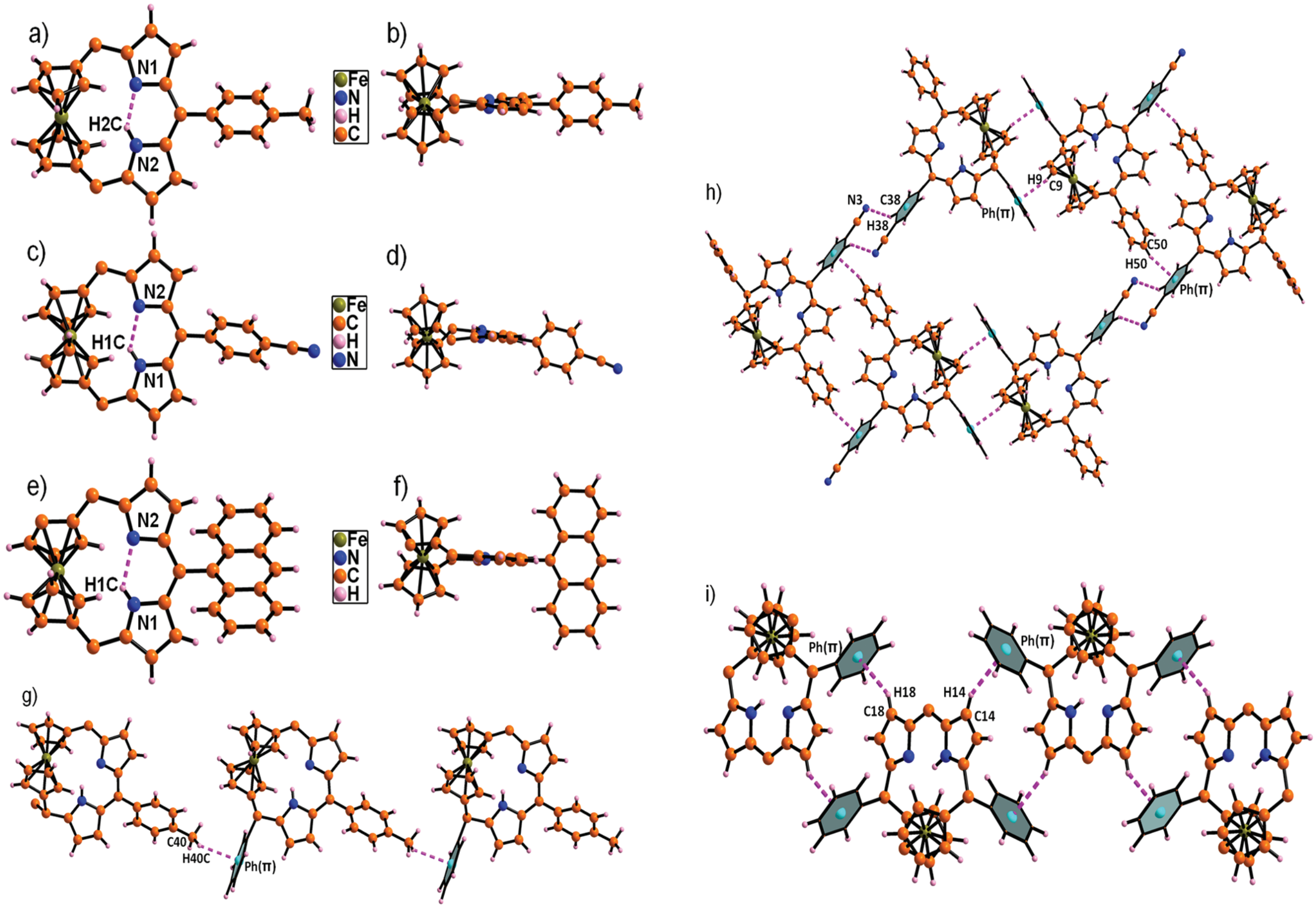


Figure 5. Single-crystal X-ray structures and analyses of **8**−**10**. (a, b; c, d; and e, f) Top and side views of **8**−**10** with intramolecular hydrogen-bonding interactions. (g, i) One-dimensional arrays of **8** and **10**. (h) Two-dimensional array of **9**. *meso*-Phenyl groups and the groups that are not involved in the intermolecular hydrogen-bonding interactions are omitted for clarity.

(0.14 g, 0.6 mmol) was added, and the solution was opened to air and stirred for a further 2 h. The solvent was removed using a rotary evaporator. The crude product was purified by silica gel column chromatography (100−200 mesh), and the red fraction eluted with CH_2Cl_2/petroleum ether (15:85) was identified as **8** in 18.5% yield. Spectral data for **8**: mp >250 °C; ^1H NMR (300 MHz, $CDCl_3$, 298 K, TMS) δ 16.26 (brs, 1H; NH), 7.61 (m, 2H; phenyl CH), 7.4−7.38 (m, 9H; phenyl CH), 7.17−7.14 (m, 8H; phenyl CH), 6.96−6.93 (m, 5H; phenyl CH), 6.62−6.61 (d, *J* = 3.92 Hz, 2H; pyrrolic-β-CH), 5.81−5.80 (d, *J* = 4 Hz, 2H; pyrrolic-β-CH), 4.59 (s, 2H; ferrocenyl CH), 3.9 (s, 2H; ferrocenyl CH), 3.86 (s, 2H; ferrocenyl CH), 2.89 (s, 2H; ferrocenyl CH), 2.45 (s, 3H; CH_3); UV/vis ($CHCl_3$) λ_{max} (ε) 468.5 nm (33 000 mol^{-1} dm^3 cm^{-1}); FAB-MS (*m*/*z*) calcd for $C_{52}H_{40}FeN_2$ 748.25, obsd 748.22 (100%, M^+). Anal. Calcd (%) for $C_{52}H_{40}FeN_2$: C 83.42, H 5.38, N 3.74. Found: C 83.31, H 5.30, N 3.69.

*Synthesis of **9**.* The above procedure was followed using 4-cyanobenzaldehyde (0.04 g, 0.3 mmol). The red fraction eluted with CH_2Cl_2/petroleum ether (40:60) was identified as **9** in 17% yield. Spectral data for **9**: mp >250 °C; ^1H NMR (300 MHz, $CDCl_3$, 298 K, TMS) δ 16.18 (brs, 1H; NH), 7.78 (s, 4H; phenyl CH), 7.38 (s, 10H; phenyl CH), 7.17−7.15 (t, 6H; phenyl CH), 6.96−6.95 (m, 4H; phenyl CH), 6.48−6.47 (d, *J* = 4.04 Hz, 2H; pyrrolic-β-CH), 5.87−5.85 (d, *J* = 3.8 Hz, 2H; pyrrolic-β-CH), 4.57 (s, 2H; ferrocenyl CH), 3.97 (s, 2H; ferrocenyl CH), 3.86 (s, 2H; ferrocenyl CH), 2.93 (s, 2H; ferrocenyl CH); UV/vis ($CHCl_3$) λ_{max} (ε) 467.4 nm (38 000 mol^{-1} dm^3 cm^{-1}); FAB-MS (*m*/*z*) calcd for $C_{52}H_{37}FeN_3$ 759.23, obsd 758.80 (100%, M^+). Anal. Calcd (%) for $C_{52}H_{37}FeN_3$: C 82.21, H 4.91, N 5.53. Found: C 82.15, H 4.97, N 5.41.

*Synthesis of **10**.* The above procedure was followed using 9-anthraldehyde (0.6 g, 0.3 mmol). The red fraction eluted with CH_2Cl_2/petroleum ether (20:80) was identified as **10** in 19% yield. Spectral data for **10**: mp >250 °C; ^1H NMR (300 MHz, $CDCl_3$, 298 K, TMS) δ 16.41 (brs, 1H; NH), 8.55 (s, 1H; phenyl H), 8.17−8.05 (m, 4H; phenyl H), 7.48−7.39 (m, 14H; phenyl H), 7.14−7.12 (m, 6H; phenyl H), 6.96−6.93 (m, 4H; phenyl H), 5.98−5.97 (d, *J* = 4 Hz, 2H; pyrrolic-β-CH), 5.69−5.67 (d, *J* = 4 Hz, 2H; pyrrolic-β-CH), 4.76 (s, 2H; ferrocenyl CH), 4.01 (s, 2H; ferrocenyl CH), 3.90 (s, 2H; ferrocenyl CH), 3.02 (s, 2H; ferrocenyl CH); UV/vis ($CHCl_3$) λ_{max} (ε) 474.5 (190 000), 386 (94 000), 366.5 (95 700), 348.5 (71 000), 332 nm (49 700 mol^{-1} dm^3 cm^{-1}); FAB-MS (*m*/*z*) calcd for $C_{59}H_{42}FeN_2$ 834.23, obsd 834.08 (100%, M^+). Anal. Calcd (%) for $C_{59}H_{42}FeN_2$: C 84.88, H 5.07, N 3.36. Found: C 84.75, H 5.13, N 3.27.

*Synthesis of **11**.* To a 250 mL flask containing **2** (0.2 g, 0.3 mmol) and **5** (0.091 g, 0.3 mmol) was added 120 mL of dry CH_2Cl_2, and the mixture was allowed to stir for 10 min at room temperature under N_2 atm. Then TFA (0.005 mL, 0.06 mmol) was added, and the solution allowed to stir for a further 2 h. To the reaction mixture was added 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (0.136 g, 0.6 mmol), and the solution was opened to the air and stirred for a further 2 h. After removal of the solvent, the crude product was purified by silica gel column chromatography (100−200 mesh). The first fraction eluted with CH_2Cl_2/petroleum ether (50:50) was identified as red solid **11** in 4% yield. Spectral data for **11**: mp >250 °C; ^1H NMR (500 MHz, $CDCl_3$, 298 K, TMS) δ 7.37 (m, 10H; phenyl CH), 7.26−7.22 (m, 10H; phenyl CH), 7.06−7.05 (m, 6H; phenyl CH), 6.84−6.83 (m, 4H; phenyl CH), 6.78−6.77 (d, *J* = 4.5 Hz, 2H; pyrrolic-β-CH), 6.74 (s, 2H; thienyl-β-CH), 6.64−6.63 (d, *J* = 4.5 Hz, 2H; pyrrolic-β-CH), 5.86 (s, 2H; ferrocenyl CH), 4.14 (s, 2H; ferrocenyl CH), 3.66−3.65 (d, J = 1 Hz, 2H; ferrocenyl CH), 3.01 (s, 2H; ferrocenyl CH); UV/vis ($CHCl_3$) λ_{max} (ε) 494.8 (38 000), 520 nm (41 000 $mol^{-1}dm^3cm^{-1}$); FAB-MS (m/z) calcd for $C_{62}H_{46}FeN_2S$ 904.26, obsd 904.68 (100%, M^+). Anal. Calcd (%) for $C_{62}H_{46}FeN_2S$: C 82.11, H 5.11, N 3.09. Found: C 82.01, H 5.09, N 3.04.

X-ray Crystallography. The single-crystal X-ray diffraction data of **8**−**11** were collected on a Bruker SMART Apex diffractometer equipped with a CCD area detector at 100(2) K, whereas those of **6** were collected on a Bruker AXS Kappa Apex 2 CCD diffractometer at 293(2) K. The data were refined by full-matrix least-squares procedures with anisotropic thermal parameters for the non-hydrogen atoms. The hydrogen atoms were calculated in ideal positions. Structures were solved by using the Crystal Structure crystallographic software package[33] and SIR97[34] and refined by full-matrix least-squares on F^2 with anisotropic displacement parameters for the non-hydrogen atoms using SHELXL-97.[35] Good-quality single crystals were grown by slow evaporation of n-heptane into $CHCl_3$ solutions of **6** and **8**−**11**. CCDC-816067 for **6**, -816068 for **8**, -816065 for **9**, -816064 for **10**, and -816066 for **11** contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

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■ AUTHOR INFORMATION

Corresponding Author

*E-mail: srini@niser.ac.in. Fax: (+91)674-2302436.

Notes

The authors declare no competing financial interest.

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