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J. Org. Chem., **Just Accepted Manuscript** • DOI: 10.1021/acs.joc.7b02095 • Publication Date (Web): 17 Oct 2017

Synthesis of Stable [28π] *m*-Benzihexaphyrins (1.0.0.1.1.1)

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Abstract

Four new expanded [28π] *m*-benziporphyrins (1.0.0.1.1.1) were synthesized by [3+3] condensation of 10,10'-bis[(*p*-toly)hydroxymethyl]-1,3-bis(2-thienyl)benzenediol with various 16-tripyrranes such as 16-thiatripyrrane, 16-oxatripyrrane, 16-azatripyrrane and 16-selenatripyrrane under mild trifluoroacetic acid catalyzed reaction conditions. The macrocycles are freely soluble in common organic solvents and their identities were confirmed by HR-MS and detailed 1D and 2D NMR spectroscopy. The macrocycles showed one sharp Soret type band at ~500 nm and broad ill-defined Q-type band(s) in the region of 600-950 nm which supports their non-aromatic nature. Upon protonation, the macrocycles exhibited bathochromically shifted absorption bands with distinct change in the colour of the solutions. The preliminary studies carried out with one of the macrocycles indicated that the macrocycles have weak tendency to form coordination complexes.

Introduction

Porphyrins are tetrapyrrolic macrocyclic ligands which possesses very rich coordination chemistry and binds almost all metals in the periodic table.[1] Carbaporphyrinoids are porphyrin analogues that possess at least one CH unit replacing a pyrrolic nitrogen in the coordination core.[2] Carbaporphyrinoids with internal carbon donor along with nitrogen donors provides a platform to afford rare organometallic complexes of transition metals in atypical oxidation states or unusual coordination geometries.[2] Carbaporphyrinoids can be derived from porphyrins by two following ways: (1) pyrrole confusion- one way of introducing carbon in the core is placing one of the pyrrolic nitrogens on the periphery of the macrocycle rather than in the core as shown in structure **A**.[2e] The pyrrole confusion increases the number of potential donor atoms because both the inner carbon and the outer nitrogen can participate in binding metal ions. (2) The insertion of carbocyclic ring- the other way of introducing carbon in the core is by replacing one of the pyrrole rings with carbacycles such as cyclopentadiene, benzene, cycloheptatriene, azulene etc as shown in structure **B**.[2f] The pyrrole confused or N-confused porphyrins were discovered independently by Furuta[3] and Latos-Grazynski research groups[4] in 1994 and over the years, several interesting and unusual metal complexes of confused porphyrins were prepared and explored their properties.[5] Similarly, the carbocyclic containing porphyrins were also discovered at the same time but the chemistry of these macrocycles was different from one macrocycle to another depending on the nature of carbocycle inserted.[6] Interestingly, the aromaticity of the macrocycle depends on the choice of carbocyclic ring inserted and the macrocycles where aromaticity is completely attenuated because of specific carbocyclic group can be reversed to aromatic by slight modifications on the carbocyclic group.[7] Among carbocyclic containing carbaporphyrinoids, the benziporphyrins received lot of attention since the aromaticity of these systems has several interesting aspects and most notably benziporphyrin is the first

reported example of a Huckel-Möbius aromaticity switch.[2f,8] The *β*-substituted *meta*-benziporphyrin (Structure **C**) was reported first in 1994 by Berlin and Breitmaier[9] but found to be very unstable in solution to study their metal coordination properties. Stepien and Latos-Grazyński synthesized stable *meso*-aryl substituted *meta*-benziporphyrin[10] (III) in 2001 and their properties including metal coordination were explored. The studies indicated that the *meta*-benziporphyrin macrocycle was nonaromatic because of incompatibility between the porphyrinoid and benzenoid delocalization modes. Latos-Grazyński et al subsequently synthesized *para*-benziporphyrin **D** and demonstrated that the aromaticity which was lost in *meta*-benziporphyrin can be restored in *para*-benziporphyrin[11]. Lash et al. and others synthesized 2-oxybenziporphyrin **E** and other carbocyclic substituted porphyrins and explored their metal coordination properties.[12] Thus, the benziporphyrins are versatile ligands for metal coordination and several interesting metal complexes were reported over the years.

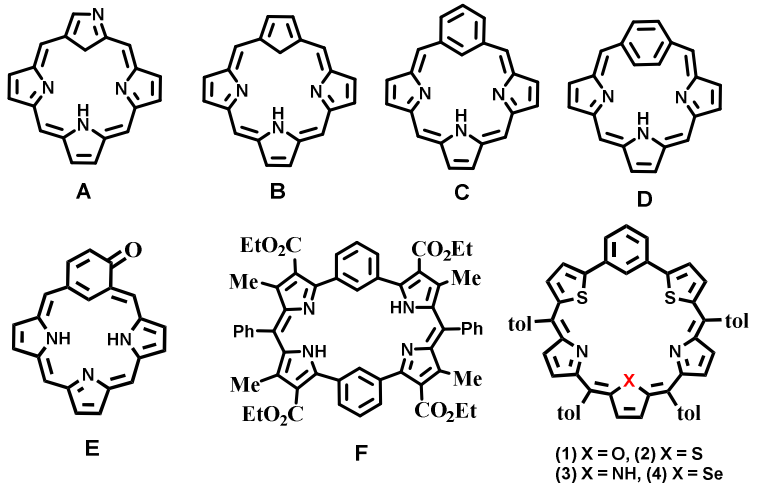


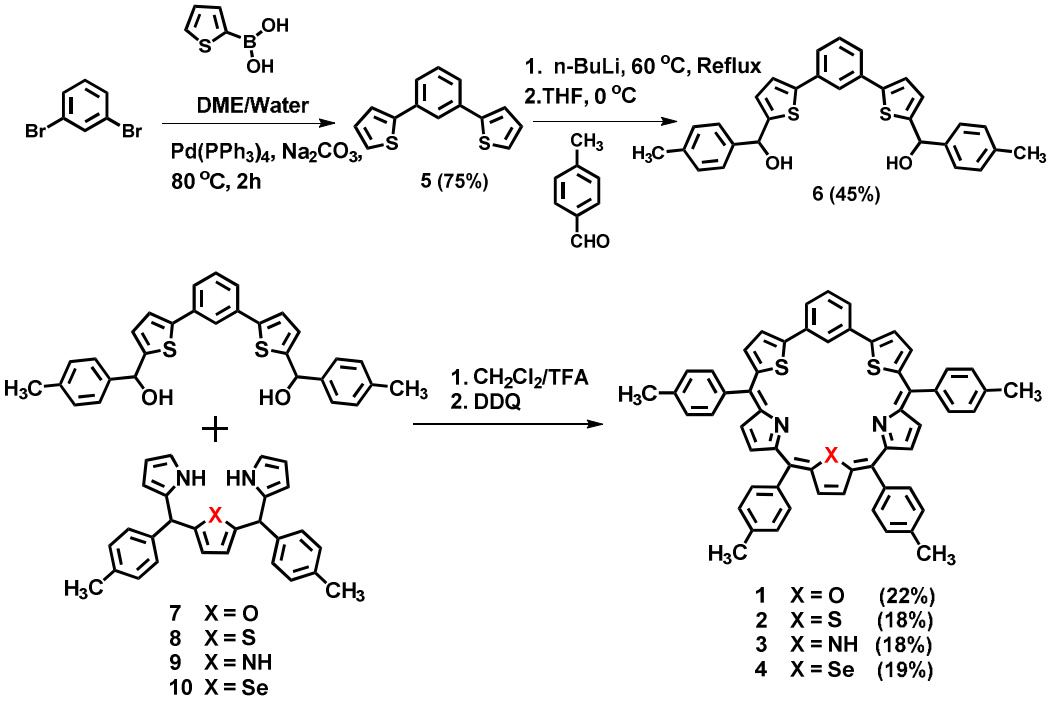
Figure 1**:** Carbaporphyrins, Benziporphyrins and expanded benziporphyrin analogues.

A perusal of literature on carbocyclic containing porphyrinoids revealed that one example of expanded *m*-benziporphyrinoid **F** was synthesized over sequence of steps by Carre et al.[13] and showed its ability to coordinate metals such as Ni(II), Pd(II) and Rh(I) ions. Recently, Setsune and co-workers have used expanded *m*-benziporphyrinoid **F** to prepare some interesting metal complexes.[14] Except these few reports, to the best of our knowledge, there is

no other report on conjugated expanded benziporphyrinoids to understand their potential for various applications. Herein, we report the synthesis of new core-modified expanded *meta*-benziporphyrinoids (**1.0.0.1.1.1**) **1-4** (Figure 1) containing N, S, O, Se and C as coordinating donor atoms under simple reaction conditions using readily available precursors. The studies showed that these macrocycles are very stable and non-aromatic 28π conjugated systems. The preliminary studies showed that the macrocycles have less potential to form coordination complexes.

Results and Discussion:

The benziporphyrinoids were always synthesized in literature using 3, 5-dicarbinol benzene as the key precursor. However, the core-modified expanded *m*-benziporphyrinoids **1-4** were synthesized by following heteroporphyrin synthetic methodology[15] as presented in Scheme 1. The key precursor, 1,3-bis(2-thienyl)benzene **5** was synthesized readily by coupling 1,3-dibromobenzene with 2-thiophene boronic acid under Suzuki coupling conditions (Scheme 1).



Scheme 1: Synthesis of benzibithia diol **6** and Benzihexaphyrins **1-4.**

The desired diol **6** was synthesized by treating compound **5** with two equivalents of *n*-butyl lithium to generate dilithiated derivative which was then treated with two equivalents of *p*-tolualdehyde in THF (Scheme 1). The formation of diol **6** was confirmed by TLC analysis which showed two major spots corresponding to mono-ol and diol **6**. The mono-ol and diol **6** mixture was separated by silica gel column chromatography using petroleum ether/ethyl acetate. The undesired mono-ol moved as the first band in petroleum ether/ ethyl acetate (90:10) and the required diol **6** was then collected as a second band in petroleum ether/ ethyl acetate (70:30) which was subsequently recrystallized from toluene to afford a white solid in 45% yield. The diol **6** was characterized by NMR, HRMS (see in Supporting Information) and elemental analysis. The molecular ion peak in mass spectrum, a sharp singlet at 6.01 ppm for -CH along with resonances corresponding to thiophene and benzene rings in ^{1}H NMR confirmed the identity of diol **6**. The other required precursors 16-oxatripyrrane **7**, 16-thiatripyrrane **8**, 16-azatripyrrane **9** and 16-selenatripyrrane **10** were synthesized by following the literature procedures.[16] The core-modified 28π expanded *m*-benziporphyrinoid (**1.0.0.1.1.1**) macrocycle **1** was synthesized by condensing one equivalent of diol **6** with one equivalent of 16-oxatripyrrane **7** by using trifluoroacetic acid as promoter under nitrogen atmosphere for 1 h followed by oxidation with DDQ in air at room temperature for additional 1 h. The TLC analysis indicated the formation of desired product as major spot along with one or two less polar minor spots corresponding to unidentified products. The desired *m*-benziporphyrinoid macrocycle **1** was separated from minor spots by basic alumina column chromatography using dichloromethane/petroleum ether (60:40) and afforded the macrocycle **1** in 22 % yield as green solid. We adopted similar approach to synthesize macrocycles **2, 3** and **4** by condensing one equivalent of diol **6** with one equivalent of appropriate tripyrrane **8, 9** and **10** respectively under same acid catalyzed conditions and obtained macrocycles **2-4** in 18-19% yields. The macrocycles **1-4** were freely soluble in

common organic solvents and their identities were confirmed by molecular ion peak in respective HR-MS mass spectra (see in Supporting Information). We attempted several times to obtain X-ray structure for one of these macrocycle but we didn't succeed in obtaining suitable crystal for analysis, However, we deduced the molecular structures of *m*-benziporphyrinoids **1-4** based on detailed 1D and 2D NMR spectra.

1D and 2D NMR spectroscopy was used to characterize the macrocycles **1-4** in detail and Figure 2 displays the ^{1}H NMR spectrum and partial ^{1}H-^{1}H COSY and ^{1}H-^{1}H NOESY spectra for macrocycle **1**. The inspection of ^{1}H NMR spectrum of macrocycle **1** indicates that the number of resonances were much less due to presence of two fold symmetry along the axis passing through the centres of heterocycle and benzene moieties. Furthermore, the heterocycle and benzene protons of macrocycle **1** were appeared in the region of 6.6 - 8.8 ppm only and no proton resonance was observed at either very downfield or upfield region indicating that the macrocycle **1** was non-aromatic. An attempt was made to identify and assign all the resonances observed in the ^{1}H NMR spectrum of macrocycle **1** based on integrated intensities of the resonances, coupling constants and proton-proton correlations observed in ^{1}H-^{1}H COSY and ^{1}H-^{1}H NOESY NMR spectra. The ^{1}H NMR spectrum of macrocycle **1** showed some doublets with coupling constant of ~8 Hz corresponding to aryl group protons and some doublets with coupling constant of ~4 Hz corresponding to heterocyclic protons of the macrocycle **1**. The ^{1}H-^{1}H COSY and NOESY spectra showed the correlations between the sets of doublet resonances which are in close proximity with each other. The inspection of ^{1}H NMR spectrum of macrocycle **1** showed two singlet resonances at 2.40 ppm and 2.48 ppm corresponding to three protons each of *meso* tolyl-CH_3 protons which we assigned as *type* I and *type* II methyl protons respectively. The *type* I methyl resonance observed at 2.40 ppm showed NOE correlation with multiplet at 7.19 ppm which we identified as *k-type meso*-aryl protons. The *k-type* protons signal at 7.19 ppm showed cross

peak correlation with doublet signal at 7.46 ppm which we identified as *l-type* aryl protons of *meso*-tolyl group. The signal at 7.46 ppm showed NOE correlation with a singlet and doublet at 8.53 ppm and 6.69 ppm which we have assigned as *a-type* and *b-type* protons respectively. The *b-type* pyrrole protons showed cross peak correlation with a signal at 6.88 ppm which was identified as *c-type* pyrrole protons. To identify the signals corresponding to other *meso*-tolyl groups, pyrrole protons and thiophene protons, we looked at NOE correlations observed for *type* II *meso*-tolyl CH_3 protons. The type II *meso*-tolyl CH_3 protons at 2.48 ppm showed NOE correlation with a doublet at 7.31 ppm which was assigned to *i-type* protons of *meso*-tolyl group. The *i-type* resonance showed cross peak correlation with a multiplet at 7.45 ppm corresponding to *j-type* aryl protons of *meso*-tolyl group. The *j-type* resonance showed NOE correlation with a signal at 7.19 ppm which was assigned as *d-type* resonance. The *d-type* resonance showed a cross peak correlation with a multiplet at 7.62 ppm which was assigned as *e-type* resonance. After we identified all *meso*-aryl and the heterocyclic ring resonances, we paid attention on remaining doublet with coupling constant of ~8 Hz corresponds to benzene moiety for two protons which we have assigned as *f-type* protons. The *f-type* protons showed cross peak correlation with a multiplet at 7.62 ppm which we have assigned as *g-type* benzene proton. The *h-type* proton of benzene ring of macrocycle which was expected to be singlet was appeared at 7.39 ppm. The macrocycles **2**-**4** also showed similar NMR features like **1** and similar strategy was employed to identify all the resonances (See in supporting information). Thus, 1D and 2D NMR spectroscopy was very useful in deducing the molecular structures of these novel macrocycles **1**-**4**.

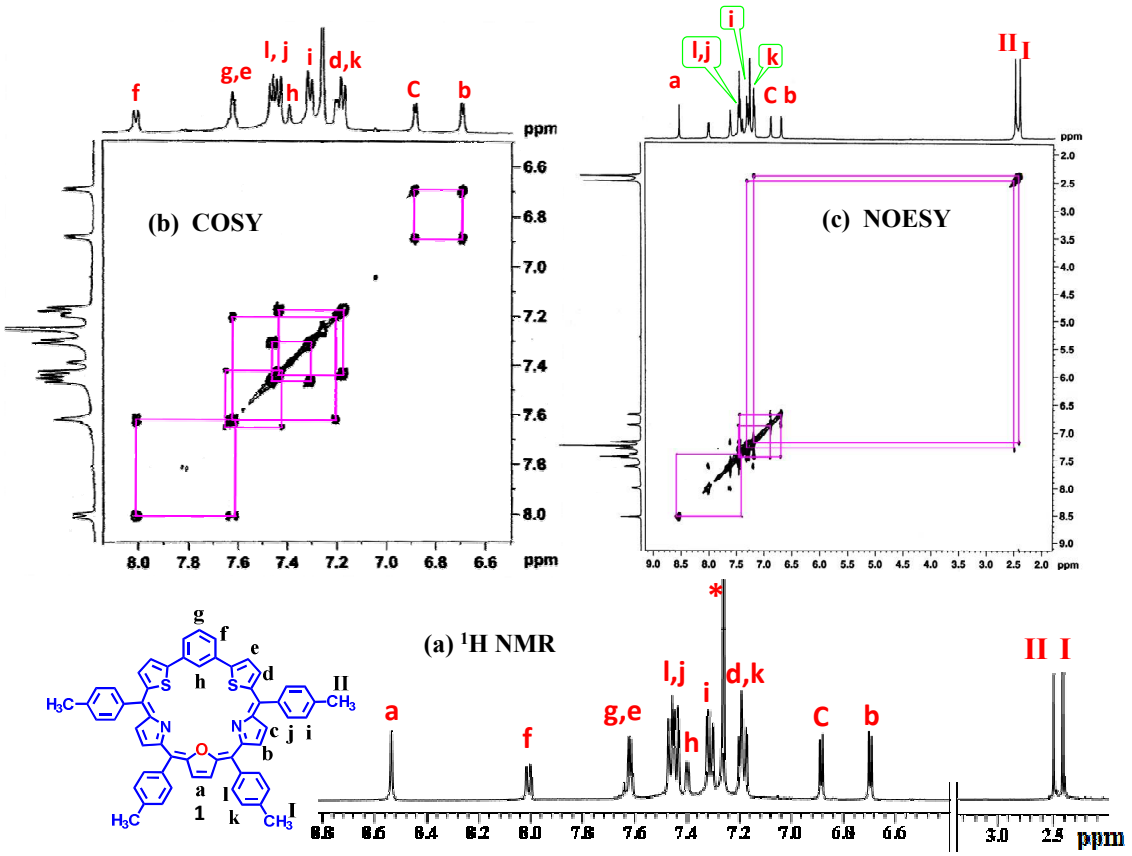
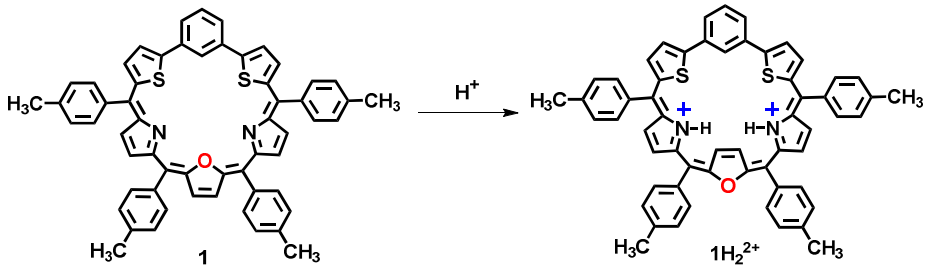


Figure 2: (a) ^{1}H NMR Spectra of compound **1**. Resonances were assigined on the basis of correlations observed in ^{1}H-^{1}H COSY (b) and ^{1}H-^{1}H NOESY (c) spectrum as shown in this figure.



Scheme 2: Protonation of compound **1**

We further carried out the NMR studies at 233 K on protonated macrocycle $\mathbf{1H_2}^{2+}$ which was generated by treating the macrocycle **1** in $CDCl_3$ with a drop of TFA as shown in Scheme 2. We noted a distinct colour change of the solution from yellowish green to red

upon protonation. The comparison of ^{1}H NMR spectra of **1** with $\mathbf{1H_2}^{2+}$ and ^{1}H-^{1}H COSY NMR spectrum of $\mathbf{1H_2}^{2+}$ are presented in Figure 3.

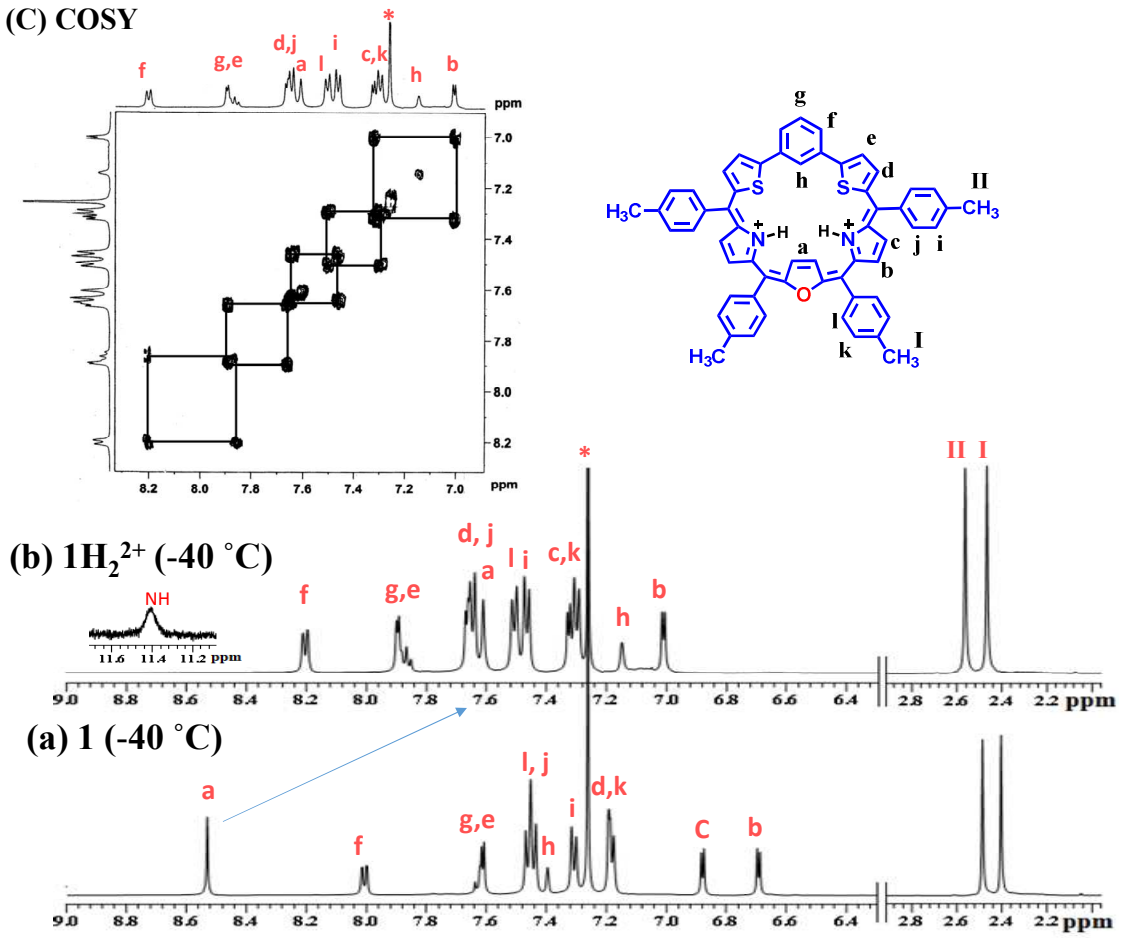


Figure 3. Comparison of ^{1}H NMR spectra of compound **1** in absence (a) and presence (b) Resonances were assigined on the basis of correlations observed in ^{1}H-^{1}H COSY (c) of traces of TFA in $CDCl_3$ at -40 ˚C.

All resonances of $\mathbf{1H_2}^{2+}$ were identified and assigned based on the correlations observed in COSY spectrum. The close inspection of figure 3 indicates that the protons of pyrrole and thiophene ring protons experienced slight downfield shifts whereas the furan protons and benzene *h-type* proton experienced upfield shifts in protonated macrocycle $\mathbf{1H_2}^{2+}$ compared to macrocycle **1**. For example, the *b-type* pyrrole protons which appeared as doublet at 6.69 ppm in macrocycle **1** was shifted downfield and appeared at 7.00 ppm,

whereas the *h-type* benzene proton which appeared at 7.39 ppm in **1** experienced upfield shift and appeared at 7.18 ppm in $\mathbf{1H_2^{2+}}$**.** Similarly, the furan *a-type* protons which appeared at 8.53 ppm in macrocycle 1 experienced an upfield shift of ~1.0 ppm and appeared at 7.60 ppm in $\mathbf{1H_2^{2+}}$**.** This large upfield shift observed for furan protons was tentatively attributed to ring flipping of furan ring upon protonation. However, the furan ring of the macrocycle may not be completely inverted but slightly tilted due to electronic and steric constraints induced upon protonation. Similar observations were made in expanded porphyrinoids.[17]

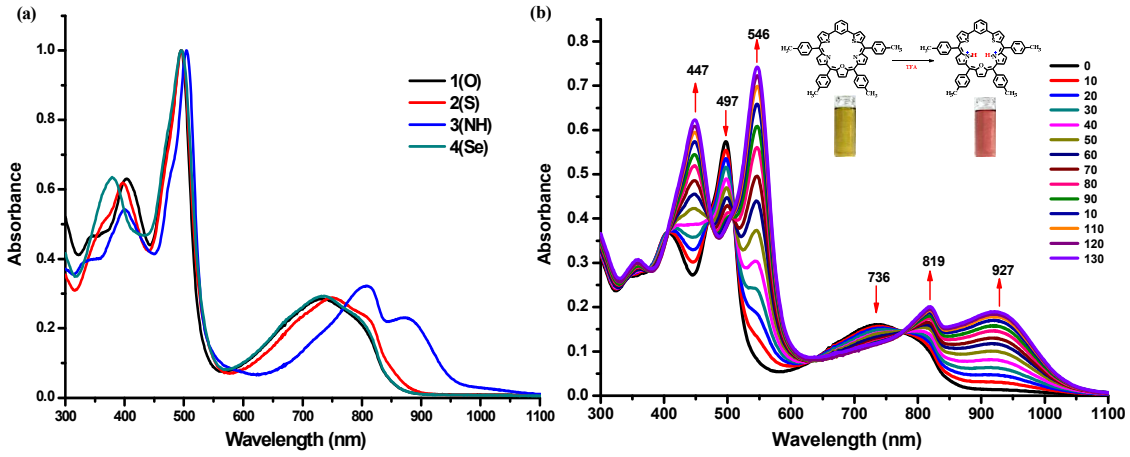


Figure 4: (a) Comparison of normalized Absorption spectra of compounds **1**-**4** in $CHCl_3$ and (b) Change in the absorption spectra of **1** (1×10^{-5} M) upon the systematic addition of (1×10^{-2} M) trifluoroacetic acid (0-130 equiv.) in $CHCl_3$.

The absorption spectra of macrocycles **1**-**4** recorded in chloroform showed one strong sharp Soret type of absorption band at ~500 nm along with a shoulder band at ~400 nm and a low-intensity broad absorption bands in the region of 600-950 nm (Figure 4a). These absorption features of macrocycles **1**-**4** were in agreement with the typical features of other nonaromatic macrocyclic systems reported in literature indicating that macrocycles **1**-**4** were nonaromatic as judged by NMR studies.[18] Among macrocycles **1**-**4**, the macrocycle **3** showed a well resolved significantly bathochromically shifted low-energy bands indicating that the π-delocalization was very effective in macrocycle **3** compared to other macrocycles (see in

Supporting Information). Upon protonation of macrocycle **1** by systematic increasing addition of trifluoroacetic acid (0-130 equiv.), the colour of the solution was changed from yellowish green to red and the absorption bands of $\mathbf{1H_2}^{2+}$ experienced bathochromic shifts with clear isosbestic points as shown in Figure 4b. Thus, these expanded *m*-benziporphyrinoids are interesting macrocycles which absorbs moderately in near infra-red region and can be used for various applications. Furthermore, we carried out preliminary studies on metal coordination potential of macrocycle **1** by treating the macrocycle **1** with various metal salts such as $PdCl_2$, $NiCl_2{\cdot}6H_2O$, $Re(CO)_5$, $Rh_2(CO)_4Cl_2$ under standard metalation conditions. Although, indications in colour change and absorption spectral changes were noticed, but we did not succeed in isolating any stable metal complex so far. Presently, the work on the potential of these macrocycles to form stable coordination complexes is under continuous study in our laboratory.

Conclusions

In summary, we synthesized and characterized the first stable nonaromatic core-modified expanded core-modified *m*-benziporphyrins (**1.0.0.1.1.1**) using readily available simple precursors. The expanded benziporphyrinoids reported here are expected to be versatile ligands for metal coordination chemistry. Since more number of donor atoms are present, these macrocycles may offer unusual binding with metals in rare oxidation state. Our preliminary studies with macrocycle **1** indicated that the macrocycle has less potential to form stable coordination complexes. However, it is now clear that various expanded benziporphyrins can be prepared readily and these types of macrocycles are now far more accessible for further investigation on their potential to form stable coordination complexes.

Materials and Methods

General Experimental: The chemicals such as $BF_3 \cdot Et_2O$ and 2, 3-dichloro-5, 6-dicyano-1,4-benzoquinone (DDQ) were used as obtained from Aldrich. All other chemicals used for the synthesis were reagent grade unless otherwise specified. Column chromatography was performed on silica gel. The ^1H NMR spectra were recorded in CDCl3 on Bruker 400 and 500 MHz instruments. The frequencies for ^{13}C nucleus are 100.06 and 125.77 MHz for 400 MHz and 500 MHz instruments respectively. Tetramethylsilane [$Si(CH_3)_4$] was used as an internal standard for ^1H and ^{13}C NMR, tetrafluorotoluene as an external standard. Absorption spectra were obtained with Shimadzu UV-Vis Spectrophotometer. The HR mass spectra were recorded with a Q-TOF micro mass spectrometer. For UV-vis titrations, the solution for all compounds (1×10^{-5} M) were prepared by using spectroscopic grade $CHCl_3$ solvent.

1,3-bis(2-thienyl)benzene 5: To the solution of 1,3-dibromobenzene (1.00 g, 4.24 mmol) and tetrakis(triphenylphosphine)palladium(0) (187 mg, 0.29 mmol) in 1,2-dimethoxyethane (30 mL), thiophene-2-boronic acid (2.17 g, 16.96 mol) was added, followed by sodium bicarbonate solution (36 mL, 1 M). The reaction mixture was heated at reflux for 4 h, with vigorous stirring under nitrogen. After completion the reaction as judged by TLC analysis, the reaction mixture was diluted with water and extracted with diethyl ether. The combined organic layers were washed with water, brine and dried over magnesium sulfate. After evaporation, the crude product was purified by silica chromatography using petroleum ether/ethyl acetate (95:5) solvent mixture to afford 1,3-bis(2-thienyl)benzene **5** as pale yellow solid (0.9 g, 87%), ^1H NMR (500 MHz, $CDCl_3$): 7.13 (dd, J = 3.6 Hz, 2H, β-Th), 7.33 (dd, J = 3.6 Hz, 2H, β-Th), 7.39-7.44 (m, 3H, Ar, β-Th), 7.55 (dd, 7.7 Hz, 2H, Ar), 7.87 (m, 1H, Ar). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 123.6, 123.7, 125.3, 128.2, 129.6, 135.2, 144.1 ppm. HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{14}H_{11}S_2$ 243.0297. found 243.0301.

10,10'-Bis[(*p*-toly)hydroxymethyl]-1,3-bis(2-thienyl)benzenediol 6: Dry, distilled n-hexane (40mL) was added to a 250-mL three-necked, round-bottom flask fitted with a rubber septum and gas inlet tube; the flask was flushed with nitrogen for 10 min. Tetramethylethylenediamine (TMEDA) (1.67 g, 2.16 mL, 14.4 mmol) and *n*-butyllithium (20 mL of ca. 15% solution in hexane) were added to the stirred solution and the reaction temperature maintained at 0° C in an ice bath. 1,3-bis(2-thienyl)benzene **5** (2.0 g, 12 mmol) was added and the solution was refluxed gently for 1 h. As the reaction progressed, a white turbid solution formed indicating the formation of lithiated salt of 1,3-bis(2-thienyl)benzene. The reaction mixture was allowed to attain room temperature. An ice cold solution of *p*-toulaldehyde (2.07 g, mL 14.4 mmol) in dry THF (40mL) was then added and stirred for an additional 15 min at 0^{o}C. The reaction mixture was brought to room temperature. The reaction was quenched by adding an ice-cold NH_4Cl solution (50 mL, ca. 1 M). The organic layer was diluted with ether and washed several times with water and brine and dried over anhydrous Na_2SO_4. The solvent was removed in a rotary evaporator under reduced pressure to afford the crude compound. TLC analysis showed three spots mainly corresponding to unchanged 1,3-bis(2-thienyl)benzene, aldehyde and the desired mono-ol. The crude compound was loaded on silica and eluted with petroleum ether. The unreacted 1,3-bis(2-thienyl)benzene and *p*-tolualdehyde were removed with petroleum ether/ethyl acetate (98: 2) solvent mixture and the desired diol **6** was collected with petroleum ether/ethyl acetate (70:30) solvent mixture. The solvent was removed in a rotary evaporator to afford diol as a white solid (45% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.36 (s, 6H), 6.01 (s, 2H), 6.85 (d, J = 3.6 Hz, 2H, β-Th), 7.15 (d, J = 3.6 Hz, 2H, β-Th), 7.18 (d, J = 8.2 Hz, 4H, Ar), 7.31 (s, 1H, Ar), 7.35 (d, J = 7.8 Hz, 4H, Ar), 7.41 (d, J = 7.8 Hz, 2H, Ar), 7.69-7.70 (m, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.3, 72.7, 123.1, 124.9, 125.8, 126.4, 129.4, 135.1, 138.1,

140.2, 143.9, 148.2 ppm. HRMS (ESI-TOF) m/z: $[M\text{-}OH]^+$ calcd for $C_{30}H_{25}OS_2$ 465.1341. found 465.1344.

10, 15, 20, 25-tetra(*p*-tolyl)-31, 35-dithia-33-oxa-benziporphyrin 1: In a 250 ml one necked round bottom flask fitted with nitrogen bubbler, samples of 10,10'-Bis[(*p*-toly)hydroxymethyl]-1,3-bis(2-thienyl)benzenediol **6** (200 mg, 0.472 mmol), 5,10-Bis(tolyl)-16-oxa-15,17-dihydrotripyrrane **7** (199 mg, 0.472 mmol), were dissolved in 200 mL of CH_2Cl_2. After purging nitrogen for 10 min, the condensation of symmetrical 1,3-bis(2-thienyl) diol **6**, tripyrrane **7** was initiated by adding TFA (0.035 mL, 0.472 mmol). The reaction mixture was stirred at room temperature for 1h. The progress of the reaction was checked by taking aliquots of the reaction mixture at regular intervals and oxidised with DDQ and recorded the absorption spectra which clearly confirmed the formation of macrocycle **1**. After 1h, DDQ (107 mg, 0.492 mmol) was added and the reaction mixture was stirred in air for additional 2 h. The solvent was removed under reduced pressure and the crude compound was purified by silica gel column chromatography. TLC analysis indicated the formation of macrocycle **1** along with other less polar undesired macrocycles. The desired macrocycle **1** was obtained as a second spot by silica gel column chromatography using petroleum ether/ dichloromethane (60:40) and afforded as a green colour solid in 22% yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.40 (s, 6H, -CH_3), 2.48 (s, 6H, -CH_3), 6.69 (d, J = 4.5 Hz, 2H, β-Py), 6.88 (d, J = 4.3 Hz, 2H, β-Py), 7.17-7.20 (m, 6H, β-Th and Ar), 7.31 (d, J = 7.7 Hz, 4H, Ar), 7.39 (s, 1H, Ar-CH), 7.43-7.46 (m, 8H, Ar), 7.61-7.63 (m, 2H, β-Th, 1H Ar), 7.99 (dd, J = 7.9 Hz, 7.8 Hz 2H, Ar), 8.53 (s, 2H, β-furan) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 21.2, 21.5, 21.6, 29.8, 114.7, 115.9, 118.5, 123.0, 124.0, 125.8, 128.4, 128.6, 129.4, 129.7, 130.9, 131.4, 131.7, 132.1, 133.4, 134.1, 135.0, 135.6, 136.1, 137.3, 138.7, 140.6, 141.6, 152.5, 153.5, 159.6, 168.4 ppm. UV-vis (in $CHCl_3$, λ_{max}/nm, *log* ε) = 405 (4.5), 497 (4.7) and 736 (4.2) HRMS (ESI-TOF) m/z: $[M]^+$ calcd for $C_{58}H_{43}N_2OS_2$ 847.2811. found 847.2811.

10,15,20,25-tetra(p-tolyl)-31,33,35-trithia-benziporphyrin 2: 10,15,20,25-Tetra(*p*-tolyl)-31, 35-dithia-33-oxa-benziporphyrin **2** was prepared by following the same procedure as given for compound **1** by using one equivalent of 10,10'-bis[(*p*-toly)hydroxymethyl]-1,3-bis(2 -thienyl)benzenediol **6** (200 mg, 0.472 mmol) and 5,10-bis(tolyl)-16-thia-15,17-dihydrotripyrrane **8** (199 mg, 0.472 mmol). The crude compound was purified by alumina column chromatography and obtained the desired macrocycle **2** using petroleum ether/ dichloromethane (60:40) as a green colour solid in 18% yield. ^{1}H NMR (400 MHz, $CDCl_3$, δ in ppm): ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.39 (s, 6H, -CH_3), 2.47 (s, 6H, -CH_3), 6.27 (d, J = 4.5 Hz, 2H, β-Py), 6.75 (d, J = 4.3 Hz, 2H, β-Py), 7.18-7.19 (m, 6H, β-Th and Ar), 7.26-7.31 (m, 8H, Ar), 7.47 (d, J = 7.3 Hz, 4H, Ar), 7.63-7.67 (m, 4H, β-Th and Ar), 8.05 (d, J = 7.2 Hz, 4H, Ar), 8.53 (s, 2H, β-furan) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 21.2, 21.5, 21.6, 29.8, 115.9, 123.9, 125.8, 128.4, 128.6, 129.2, 129.4, 129.6, 130.9, 131.4, 131.7, 132.1, 133.4, 134.9, 135.6, 136.6, 137.3, 138.7, 140.5, 141.7, 152.5, 153.5, 159.6, 168.4 ppm. UV-vis (in $CHCl_3$, λ_{max}/nm, *log* ε) = 381 (4.7), 498 (4.9) and 734 (4.3); HRMS (ESI-TOF) m/z: $[M]^+$ calcd for $C_{58}H_{43}N_2S_3$: 863.2583. found 863.2583.

10, 15, 20, 25-tetra(*p*-tolyl)-31, 35-dithia-33-aza-benziporphyrin 3: 10,15,20,25-Tetra(*p*-tolyl)-31, 35-dithia-33-aza-benziporphyrin **3** was prepared by following the same procedure as given for compound **1** by using one equivalent of 10,10'-Bis[(*p*-toly)hydroxymethyl]-1,3-bis(2-thienyl)benzenediol **6** (200 mg, 0.472 mmol), 5,10-Bis(tolyl)-16-aza-15,17-dihydrotripyrrane **9** (199 mg, 0.472 mmol). The crude compound was purified by alumina column chromatography and obtained the desired macrocycle **3** using petroleum ether/ dichloromethane (60:40) as a green colour solid in 18% yield. ^{1}H NMR (400 MHz, $CDCl_3$, δ in ppm): ^{1}H NMR (500 MHz, $CDCl_3$,): δ = 2.40 (s, 6H, -CH_3), 2.48 (s, 6H, -CH_3), 6.60 (d, J = 4.5 Hz, 2H, β-Py), 6.85 (d, J = 4.3 Hz, 2H, β-Py), 7.19-7.30 (m, 10H, β-Th and Ar), 7.39 (d, J = 8.0 Hz, 4H, Ar), 7.46 (d, J = 8.0 Hz, 4H, Ar), 7.56 (s, 1H, Ar), 7.68-7.69 (m, 3H, β-Th

and Ar), 8.11 (d, J = 7.7 Hz, 2H, Ar), 8.33 (s, 2H, β-furan) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.4, 21.5, 29.8, 115.2, 116.5, 124.0, 125.6, 128.6, 129.4, 130.9, 131.1, 131.5, 134.6, 134.8, 135.3, 136.5, 137.7, 138.4, 152.5, 153.5, 159.6, 168.4 ppm. UV-vis (in $CHCl_3$, λ_{max}/nm, *log* ε) = 402 (4.5), 506 (4.8), 808 (4.3) and 880 (4.1); HRMS (ESI-TOF) m/z: $[M]^+$ calcd for $C_{58}H_{44}N_3S_2$: 846.2971. found 846.2971.

10, 15, 20, 25-tetra(*p*-tolyl)-31, 35-dithia-33-selenium-benziporphyrin 4: 10,15,20,25-Tetra(*p*-tolyl)-31, 35-dithia-33-selenium-benziporphyrin **4** was prepared by following the same procedure as given for compound **1** by using one equivalent of 10,10'-Bis[(*p*-toly)hydroxymethyl]-1,3-bis(2 -thienyl)benzenediol **6** (200 mg, 0.472 mmol), 5,10-Bis(tolyl)-16-selenium-15,17-dihydrotripyrrane **10** (199 mg, 0.472 mmol). The crude compound was purified by alumina column chromatography and obtained the desired macrocycle **4** using petroleum ether/ dichloromethane (60:40) as a green colour solid in 19% yield. ^{1}H NMR (400 MHz, $CDCl_3$, δ in ppm): ^{1}H NMR (500 MHz, $CDCl_3$,): δ = 2.38 (s, 6H, -CH_3), 2.46 (s, 6H, -CH_3), 6.20 (d, J = 4.6 Hz, 2H, β-Py), 6.71 (d, J = 4.4 Hz, 2H, β-Py), 7.17-7.19 (m, 6H, β-Th and Ar), 7.26-7.32 (m, 9H, Ar), 7.40 (d, J = 7.4 Hz, 4H, Ar), 7.57 (d, J = 4.0 Hz, 2H, β-Th), 7.63 (t, J = 7.4 Hz, 1H, Ar), 7.99 (d, J = 8.0 Hz, 2H, Ar), 8.74 (s, 2H, β-Selenophene) ppm.. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 20.2, 20.5, 20.6, 28.8, 114.9, 117.5, 122.9, 124.8, 127.4, 127.6, 128.2, 128.4, 128.6, 129.9, 130.4, 130.7, 131.1, 132.4, 133.1, 133.9, 134.6, 135.1, 136.3, 137.7, 139.5, 140.7, 151.5 152.5, 158.5, 167.4 ppm. UV-vis (in $CHCl_3$, λ_{max}/nm, *log* ε) = 381 (4.7), 498 (4.9) and 736 (4.3); HRMS (ESI-TOF) m/z: $[M]^+$ calcd for $C_{58}H_{43}N_2S_2Se$: 911.2034. found 911.2029.

Associated Content

Supporting Information

Supporting information for this article is available on the WWW under http:// pubs.acs.org. It contains characterization data (including HRMS, ^{1}H, and ^{13}C NMR spectra) for all the reported compounds and absorption data.

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Notes

The authors declare no competing financial interest.

Acknowledgements

M.R thanks the department of Science and Technology, Govt. of India (File No. EMR/2015/002196 to MR) and S. K thanks the UGC for a fellowship.

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Graphical abstract