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The Curious Case of a Parasitic Twin of the Corroles

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Abstract: A new expanded porphyrinoid has been obtained by a simple ring expansion from a contracted porphyrinoid, *i.e.*, corrole. Spectroscopic, structural and computational investigations reveal peculiar π -conjugation and geometry. The effect of extended π -conjugation is evident from perturbed redox behavior and photophysical properties. Due to strong diatropic ring current of the corrole and cross-conjugation, the molecule exhibits non aromatic nature for the expanded π -circuit as evident from NMR studies.

Expanded porphyrinoids^[1] have been gaining remarkable attention in light of their versatile attributes such as diverse π conjugation pathways due to flexible structures,^[2] near infrared (NIR) absorption/emission,^[3] facile interconversion between multiple redox-states,^[4] and multi-metal coordination cavities for various divalent and trivalent metal ions.^[5] For example, the regular hexaphyrin(1.1.1.1.1) exhibits **UV-Vis-NIR** absorption/emission^[1,3] and capable of switching between a Hückel aromatic and antiaromatic (or Möbius aromatic) species.^[6] From the perspective of coordination chemistry, the hexaphyrin(1.1.1.1.1) displays two unique 'NNCC' coordination cavities to afford bimetallic complex with various conformations owing to their inherent topological flexibility.^[4a,5a,7] Similarly, the singly and doubly N-confused hexaphyrins (I and II, Figure 1) are also very attractive candidates as NIR absorbing dyes, interconversion between multiple redox-states and multi-metal coordination ligands with unique cavities.^[8]

On the other hand, the internally bridged expanded such as hexaphyrin,^[9] octaphyrin^[11] porphyrinoids and decaphyrin^[10a] with various linkers are electronically very different owing to their multiple conjugated π -electronic pathways. As a rare example, Osuka et. al., reported internally 5,20aromatic-bridged hexaphyrin (III), which exhibits dual π conjugation consisting of [18]porphyrin and/or [26]hexaphyrin pathway.^[9a] A significant contribution of [18]porphyrin was observed in case of 2,5-pyrrylene and 2,5-thienylene bridged hexaphyrins due to the smaller dihedral angle with the tripyrromethene fragment. Similarly, the electronic structure of trans-vinylene-bridged hexaphyrin (IV) can also be considered as a [16]Annuleno[16]Annulene fused conjugated π -electronic system, nevertheless the resonance contribution is minor.^[9b]

In this direction, it will be interesting to see the effect of lateral π -extension of an existing π -electronic pathway of a

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 E-mail: sankar@iiserb.ac.in smaller porphyrinoid.^[10] To this effect, herein we report the synthesis and electronic structure of hexaphyrins (**4** and **4-Rh**, Figure 1) obtained by π -expansion of a ring contracted porphyrinoid. Alternatively, this macrocycle can also be viewed [12]



Figure 1: Structure of singly and doubly N-confused hexaphyrin (I and II), internally-aromatic-straped hexaphyrin (III), trans-vinylene-bridge hexaphyrin (IV), corrole isomer (V) and internally C-linked doubly N-confused hexaphyrins (4 and 4-Rh). The N-confused pyrroles are represented in blue colour.

The target molecule was synthesized by acid catalysed condensation reaction of (TPFC)Ga(III)(Py)-2,17-biscarbinol (2) via two routes (Scheme 1, see details in Supporting Information). The Vilsmeier-Haack formylation of (TPFC)Ga(III)(Py) (1) gave 2,17-bisformyI(TPFC)Ga(III)(Py)₂ (1b) in good yield.^[12b] 1b on reaction with phenylmagnesiumbromide in tetrahydrofuran yielded 2. Succesively, the reaction of 2 with excess of pyrrole in presence of trifluoroacetic acid (TFA) afforded the compound 3. Notably, due to the decomposition of 2 and 3 during column chromatography, these compounds were directly utilized without purification in the subsequent reactions. To achieve the target 4, 3 was reacted with 2,3,4,5,6-pentafluorobenzaldehyde in dichloromethane (CH₂Cl₂) followed by oxidation with 2,3dichloro-5,6-dicyano-1,4-benzoquinone (DDQ). Repeated purification by silica gel and size exclusion gel permeation column chromatography gave 4 in 5% yield as the only isolable product. High resolution mass spectrometry-electron-spray ionization (HRMS-ESI) showed parent ion peaks at m/z = 1426.1284 (calculated for C71H26F20GaN7: 1426.1259 [M+H]⁺) and 1347.0834 (calculated for C₆₆H₂₁F₂₀GaN₆: 1347.0837 [M+H-Py]⁺).

Alternatively, an improvement in the yield was observed upon direct condensation of **2** with 2,3,4,5,6pentafluorophenyldipyrromethane in presence of TFA. We could achieve a yield of 18% with 1:1 molar ratio of **2** and 2,3,4,5,6pentafluorophenyldipyrromethane under dilute condition (0.05 mM) and TFA (0.3 equiv.) as catalyst for 3 hours. In fact, the similar product conversion was also observed with borontrifluoride diethyletherate (BF₃.OEt₂). COMMUNICATION

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Scheme 1: Synthesis of 4 and 4-Rh: (a) GaCl₃ (50 equiv.), pyridine, 100°C, Ar, 2 hrs, 82%; (b) POCl₃/DMF (100 equiv.), 0°C, Ar, 2 hrs, K₂CO₃ (aq), 12 hrs, 70 %; (c) PhMgBr (10 equiv.), THF, rt, Ar, 2 hrs, quantitative yield; (d) pyrrole (100 equiv.), TFA (0.3 equiv.), CH₂Cl₂, rt, Ar, 2 hrs; (e) 2,3,4,5,6-pentafluorobenzaldehyde (1 equiv.), TFA (0.3 equiv.), CH₂Cl₂, 0.05 mM, rt, Ar, 3 hrs, pyridine, DDQ (1.5 equiv.), 1 hour, 5%; (f) TFA (0.3 equiv.), CH₂Cl₂, 0.05 mM, rt, Ar, 3 hrs, pyridine, DDQ (1.5 equiv.), 1 h, 18%; (g) [Rh(CO)₂Cl]₂ (5 equiv.), CH₃COONa (10 equiv.), CH₂Cl₂, Ar, 1 h, 50°C, 90%.

However, the TFA-catalysed reaction was found to be consistent in the reproducibility of the reaction. The dipyrromethene fragment of corrorin isomer unit in **4** can offer a monoanionic coordination environment. Thus, **4** was treated with reagents such as BF₃.OEt₂/Et₃N^[14a] and POCl₃/pyridine.^[14b] However, these attempts did not yield any metallated complexes. Rh(I) had been shown earlier to exhibit out of plane coordination mode along with two carbonyl ligands.^[15] Interestingly, the reaction of **4** with [Rh(CO)₂Cl]₂ in DCM at 50°C for 2 hours gave **5** in 90% yield (Scheme 1), which decomposes gradually in solution during crystallization. The HRMS-ESI revealed molecular ion peak at m/z = 1583.0075 (calculated for C₇₃H₂₅F₂₀GaRhO₂N₇: 1583.0056 [M]⁺).

¹H NMR spectrum in CDCl₃ indicated an unsymmetrical structure for **4**, which exhibits two singlets (δ 9.52 and 8.38 ppm, bipyrrolic β -H) and four doublets (δ 8.81, 8.66, 8.53 and 8.43 ppm; ${}^{3}J_{H-H} \sim 4.6$ hz, pyrrolic β -H) as assigned to the Ga(III)corrole unit (Figure 2a). The β -Hs of dipyrromethene fragment of corrorin unit resonate as four doublets (& 7.54, 7.20, 6.83 and 6.45 ppm; ${}^{3}J_{H-H} \sim 5.2$ hz). The downfield resonance of β -Hs reflected a diatropic ring current for Ga(III)corrole unit, which is similar to that observed for [18] π -electronic corrole or porphyrin.^[16] On the other hand, the corrorin unit resembled a non-aromatic core (vide infra). A broad peak at δ 11.86 ppm was assigned to internal NH proton and was confirmed by deuterium exchange experiment (Figure S14, see Supporting Information). The relatively larger downfield resonance of NH proton can be attributed to the presence of intramolecular hydrogen bonding. In addition, the NH proton can easily be deprotonated with tetrabutylammonium fluoride (TBAF) as observed by ¹H NMR titration experiment (Figure SI15). The compound 4-Rh exhibits similar ¹H NMR spectrum as compound 4 except for the noticeable upfield resonance for inner β -H of corrorin isomer unit (Figure 1b). The β -H of 4 and 4-Rh were correlated and assigned on the basis of ¹H-¹H COSY and ¹H-¹H NOESY spectra (Figure S10 and Figure S13). The NMR investigations





Figure 3: Single crystal X-ray structure of **4**, (a) top view and (b) side view. Hydrogen atoms are omitted for clarity. DFT optimized structure of **4-Rh**, (d) top view and (e) side view. Interplanar angle between 24-atom mean-plane of Ga(III)corrole unit (red) and 11-atom mean-plane of dipyrromethene fragment (blue) in **4** (c) and **4-Rh** (f) respectively.

support the absence of an aromatic ring current inside the corrorin isomer unit while maintaining a strong local diatropic current for the Ga(III)corrole ring.

The structure of **4** was confirmed by single crystal X-ray diffraction analysis obtained from slow evaporation of a DCM solution containing small amount of pyridine at low temperature.^[17] Unexpectedly, the geometry of hexaphyrin framework has adopted a non-planar conformation owing to the out of plane deviation of dipyrromethene fragment of corrorin isomer unit (Figure 3). This is probably due to the smaller cavity of corrorin isomer core to accommodate two inner hydrogens (i.e., NH and CH each), and steric hinderance amongst the *meso*-aryl substituents at 15C and 20C having centroid to centroid distance of roughly 3.60 Å. Notably, this spatial proximity was clearly evident in solution as inferred from the broad aryl ¹H and ¹⁹F resonances.

The electronic structure of **4** and **4-Rh** were investigated by density functional theory (DFT) calculation with Gaussian 09/D.01 at the B3LYP/6-31G* (C, H, N, F) + LANL2DZ (Ga/Rh) level.^[18] Despite the reduced symmetry for **4** and **4-Rh**, computations suggested the presence of near-degenerate pairs COMMUNICATION

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of HOMOs and LUMOs as commonly observed in the case of symmetrical porphyrin (D_{4h}) or corrole (C_{2v}) macrocycles (Figure S21). $^{[19]}$



Figure 4: (a) Possible resonance ([18] π -electron and [26] π -electron) of 4 (4-Rh) and conjugation in ref. Dipyrromethene. The conjugation pathways are presented in bold black line and cross-conjugation is presented in red line. (b) NICS(0) values at various point of 4 and ref. dipyrromethene calculated at B3LYP/6-31G* (C, H, N, F) + LANL2DZ (Ga/Rh) level. (c) HOMA values of 4 and 4-Rh. ^aout of plane calculated NICS value owing to the non-planar conformation.

Furthermore, in order to probe the aromaticity for 4 and 4-Rh, nucleus-independent chemical shift (NICS),^[20] anisotropy-of the induced current density (ACID)^[21] and harmonic oscillator model for aromaticity (HOMA)^[20] were calculated (Figure 4). Inside Ga(III)corrole unit of 4, the calculated NICS(0) values were all large and negative (-17.8, -15.1, -15.8 and -15.2) indicating the intact aromatic character of Ga(III)corrole core. The corrorin isomer core exhibited moderately negative NICS values in all calculated regions (-3.9, -7.2, -2.3 and -7.4), which is only slightly larger than the values obtained for ref. dipyrromethene fragment (Figure 4b). The AICD plot showed a strong clockwise current flow in Ga(III)corrole unit and absence of any recognizable directional current flow on the dipyrromethene fragment of the corrorin isomer unit (Figure S21). This suggests a non-aromatic [26] π -electronic hexaphyrin contribution and a strongly localized aromatic character of [18] π electronic Ga(III)corrole core. In addition, the [18]Ga(III)corrole unit and [26]hexaphyrin π -circuit exhibit HOMA value of 0.589 and 0.506 respectively in 4 (Figure 4c).^[17] The computational results further substantiated with the observed downfield signal for inner β -H in 4 (δ = 9.52 ppm) and 4-Rh (δ = 8.23 ppm). Probably, the non-aromatic character of [26] π -electronic hexaphyrin is due to the cross-conjugation^[22] at the bipyrrole unit (Figure 4a) and non-planarity of the dipyrromethene fragment. Notably, the inner β -H for **4-Rh** appeared more shielded roughly by 1.25 ppm as compared to 4. This is most likely due to the improved co-planarity of dipyrromethene fragment and Ga(III)corrole core in 4-Rh having interplanar angle of roughly 12.7° than that of 4 with interplanar angle of roughly 28.9° (Figure 3c and Figure 3f). This induces an upfield resonance for inner β -H due to the slight enhancement of conjugation of [26] π electronic circuit in 4-Rh. Nevertheless, we believe a nonaromatic [26] π -electronic hexaphyrin and a strongly aromatic Ga(III)corrole unit.

The electronic absorption spectrum (Figure 5) of **4** in DCM showed a Soret-type band at 433 nm (ϵ = 1.3x 10⁵ M⁻¹cm⁻¹) and a weaker broad Q-type band spanning roughly 500-800 nm

spectral window ($\lambda_{max} = 600 \text{ nm}$; $\varepsilon = 0.4 \times 10^5 \text{ M}^{-1} \text{ cm}^{-1}$), which is akin to those characteristic of Ga(III)corrole^[12] but indicated slightly extended π -conjugation as evident from the red shifted spectra. Furthermore, it exhibited a sharp emission at $\lambda_{max} \sim 605$ nm along with a shoulder peak ($\lambda \sim 660 \text{ nm}$). In fact, the emission is corrole centered, which further supported the intact aromatic character of Ga(III)corrole unit. The absolute quantum yield of 4 was measured to be 1.3%. The electronic absorption spectra of 4-Rh in DCM exhibited similar pattern as 4 but slightly red shifted. The emission in 4-Rh was found to be quenched completely due the internal heavy atom effect.







Figure 6: (a) Molecular structure of chlorinated species [4-CI] after oxidation of 4 with Magic Blue. (b) UV-Vis-NIR spectral change of 4 with gradual addition of tris(4-bromophenyl)ammoniumyl hexachloroantimonate in acetonitrile. (c) X-band ESR spectra of in-situ generated radical [4-CI] in toluene/DCM (1:1, v/v) at 110 K. (d) Spin density of [4-CI] calculated at RB3LYP/6-31G*(C, H, N, F, CI) + LANL2DZ (Ga).

Cyclic voltammetry (CV) and differential pulse voltammetry (DPV) of **4** (Figure S23 and Figure S24) in DCM showed three oxidation processes at the potential (*vs* SCE) 0.53 V (rev.), 0.82 V (quasi rev.) and 1.01 V (quasi rev.), and two reduction processes at potential -1.10 V (irrev.) and -1.20 V (irrev.). The first oxidation potential of **4** is shifted cathodically by about ~300 mV with respect to (TPFC)Ga(III)(Py),^[12a] suggesting an extended π -electronic conjugation. Similarly, the **4-Rh** (Figure S23 and Figure S24) showed three oxidation potential waves at 0.43 V (rev), 0.77 V (quasi rev.) and 1.12 V (quasi rev.), and two reduction potential waves at 1.10 V (irrev) and 1.27 V (irrev). The **4-Rh** has smaller electrochemical HOMO-LUMO gap of 1.53 eV than that of **4** (1.73 eV). The smaller energy gap of **4-Rh** was also evident from the moderately red shifted electronic absorption spectra. This may stem from the enhanced

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unit.

coplanarity of the dipyrromethene moiety to the Ga(III)corrole

Furthermore, to verify the electronic nature of the intact π circuit of Ga(III)corrole, 4 was treated with one electron oxidizing tris(4-bromophenyl)ammoniumhexachloroantimonate agent (Magic Blue, E_{1/2}= 1.1 V Vs SCE) in acetonitrile $^{\left[12a,23\right]}$ and spectral change was monitored by UV-Vis-NIR spectroscopy (Figure 6b). It exhibited a blue shifted Soret-type band (~400 nm), diminished Q-type band and new broad near-infrared absorption (~1070 nm). The X-band ESR spectrum of 4 on reaction with Magic Blue reveals the formation of a radical with $g_{iso} = 2.0057$ in toluene/DCM (1:1, v/v) at 110 K (Figure 6c). As expected, the HRMS-ESI analysis showed a molecular ion peak at m/z = 1381.0441 (Figure S20), which can be attributed to a chlorinated radical [4-CI] having empirical formula of $C_{66}H_{21}F_{20}CIN_6Ga$ (1381.0447[M]⁺). The structure of chlorinated radical [4-CI] was assigned on the basis of mass-spectrometry analysis and supported from the previous report,^[23] where a chlorine ion was found to be coordinated to the Ga(III) ion (Figure 6a). The singly occupied molecular orbitals (SOMOs) and spin density distribution plot of compound [4-CI] showed that the electron density of unpaired electron is distributed over entire π -system of hexaphyrin (Figure S25 and Figure 6d) with no contribution from the Ga(III) centre, which is also consistent with the isotropic ESR signal.

In summary, a strategically new expanded porphyrinoid having corrole and a corrorin isomer unit onto a single framework has been achieved by π -expansion of corrole. The NMR investigations reveal an interesting behavior of diatropic and cross-conjugated circuit within the same macrocycle. Computational investigations supported the experimental and structural observations. The ability of the molecules to metallate Rh(I) into the corrorin isomer ring system is demonstrated. The facile oxidation of the molecules has been exploited to observe the formation of a radical on one electron chemical oxidation. Due to the presence of a dominating diatropic current for corrole and non aromatic nature of corrorin, it is named as a parasitic twin as both corrole and corrorin are isomers. The current work demonstrates that this simple π -expansion strategy via condensation could be beneficial to access many more such interesting molecules in the future.

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 π -expansion of a Ga(III)[18]corrole yields a novel hexapyrrolic expanded porphyrinoid with aromatic and cross-conjugated π -circuit in a single molecular framework.



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