Dicarbacorrole

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A 6,11,16-Triarylbiphenylcorrole with an *adj*-CCNN Core: Stabilization of an Organocopper(III) Complex**

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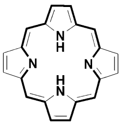
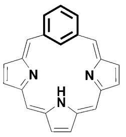
Dedicated to Professor T. K. Chandrashekar

Abstract: *An adj-dicarbacorrole with CCNN in the core is achieved by replacing the bipyrrole moiety by a simple polycyclic aromatic hydrocarbon, such as biphenyl unit. Spectroscopic studies and structural analyzes confirm the absence of macrocyclic aromatization, thus leading to overall nonaromatic character. The trianionic core is effectively utilized to stabilize a copper(III) ion to form an organocopper complex.*

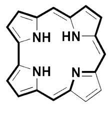
The porphyrin **1** is highly aromatic and contains 18π electrons in the delocalization pathway with a NNNN core.[1] Carbaporphyrinoid is a porphyrin analogue in which one or more nitrogen atoms in the porphyrin core is replaced by carbon atoms and receiving much attention in recent years.[2] Research has mainly focused on monocarbaporphyrinoids with CNNN in the core, which includes N-confused porphyrins,[3] benziporphyrins,[4] oxybenziporphyrins,[5] tropiporphyrins,[6] benzocarbaporphyrins,[7] azuliporphyrins,[8] N-confused pyriporphyrins,[9] O- and S-confused heteroporphyrins,[10] pyrazoloporphyrins,[11] napthiporphyrins,[12] and neo-confused porphyrins.[13] The slight modification in the framework 1) leads to unusual reactivity and spectral properties; 2) provides information about the nature of porphyrinoids aromaticity; and 3) generates organometallic complexes with unusual oxidation states.[2–13] Depending on the nature of the aromatic subunits in the framework, the degree of aromaticity varies. For example, benzocarbaporphyrins[7] are highly aromatic; azuli derivatives[8] are weakly aromatic, whereas the *m*-benziporphyrin (**2**)[4b] is nonaromatic. However, compared to monocarbaporphyrinoids, only limited number of dicarbaporphyrinoids with *cis*- or *adj*-CCNN and *trans*- or *opp*-CNCN in the core is known. This includes aromatic *cis*- and *trans*-doubly N-confused porphyrins, which form organo-Cu^{III} and Ag^{III} complexes.[14] Among the dicarbaporphyrins with *opp*-two indene units,[15] *opp*-[16a]/*adj*[16b,c]-azulene and indene units, and *adj*-diazuli derivatives,[17] only the last two macrocycles are stable. Recently reported stable aromatic *adj*-dicarbaporphyrins with two indene units forms a tripalladium sandwich complex.[18] The very recently described phenanthriporphyrin with *adj*-CCNN in the core is an antiaromatic aceneporphyrinoid, which affords a hypervalent organophosphorus(V) complex.[19]



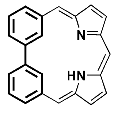
1
(NNNN)



2
(CNNN)



3
(NNNN)



4
(*adj*-CCNN)

On the other hand, by removing one of the *meso* carbon atoms in the framework of porphyrin **1** leads to contracted porphyrinoids such as corrole **3** (NNNN), which stabilizes the unusually high-oxidation-state transition-metal complexes.[20] As compared to monocarbaporphyrinoids, the number of monocarbacorroles (CNNN) is fewer, and these include isocarbacorrole,[21] the series of N-confused corroles,[22] norrole, and benzocorrole.[23] The non-aromatic isocarbacorrole stabilizes organo-Cu^{III} and Ag^{III} complexes,[21] while the aromatic N-confused corroles bind effectively with anions.[22] However, the next level in the carbacorrole chemistry, dicarbacorrole with the core containing *adj*-CCNN or *opp*-CNCN framework is not known to date. Such a macrocycle would have an ideal platform to stabilize higher-oxidation-state organometallic complexes, as observed in the porphyrin analogues. Herein, we wish to report the synthesis of an *adj*-dicarbacorrole with CCNN in the core, termed 6,11,16-triarylbiphenylcorrole **4** or A,D-di-*m*-benziporphyrin(1.1.1.0). A formal conversion of **3** into **4** is achieved by introducing a biphenyl unit in place of bipyrrole unit in **3**. Based on the spectral studies and structural characterization, the macrocycle **4** is found to be nonaromatic and the trianionic core best suit for the Cu^{III} metal ion to form the organocopper complex.

The synthesis of the target macrocycle and its metal complex is outlined in Scheme 1, where the synthesis involved three steps. The first step is the conversion of biphenyl-3,3′-dicarbaldehyde (**6**)[24] to 3,3′-bis(phenylhydroxymethyl)bi-

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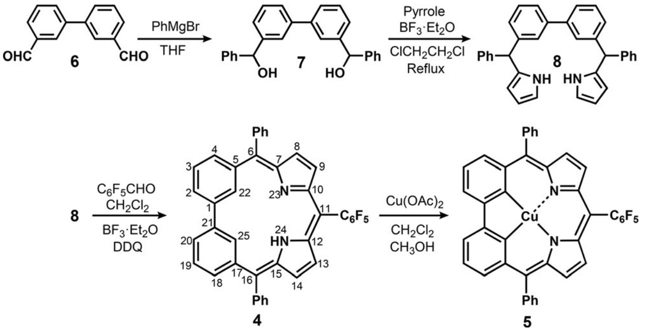

Scheme 1. Synthesis of **4** and **5**.

phenyl (**7**) by using freshly prepared Grignard reagent such as phenylmagnesium bromide in THF to afford **7** in 65% yield. The key precursor, 3,3′-biphenyl-bis(dipyrromethane) **8**, was synthesized in the second step by condensing **7** with an excess of pyrrole in presence of $BF_3 \cdot Et_2O$, where the direct conversion was not successful, hence, we followed a similar strategy as reported by Latos-Grażyński et al,[25] where the mixture was refluxed for 8 h by using 1,2-dichloroethane as solvent to afford **8** in 42% yield. In the final step, we followed the Lindsey macrocyclization procedure,[26] where the $BF_3 \cdot Et_2O$ acid-catalyzed condensation reaction of **8** with pentafluorobenzaldehyde followed by oxidation with 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ) afforded **4** in 10% yield. The compound was characterized by standard analytical techniques and further confirmed by single crystal X-ray diffraction analysis. The electron spray ionization (ESI) mass spectral analysis of **4** exhibits the molecular ion peak at *m*/*z* 639.1821 [M+1] (Supporting Information, Figure S4) and is consistent with the exact composition of the macrocycle.

The electronic absorption spectral analysis of **4** in its freebase and protonated form is shown in Figure 1. The freebase form exhibits an intense band at 367 nm and broad absorption bands at 612 nm and 644 nm with the molar absorption coefficient ε of 10^5. Comparisons of these data with **2** and **3** reveal the following: 1) the similar intense absorption band and the ε value is in the order of 10^5, as observed in **2**,[4b] suggests the nonaromatic character in **4**; however reduction in the π-electron delocalization is observed in **4**, where the intense band is blue shifted by 44 nm (tripyrromethene in **2** vs dipyrromethene in **4**); and 2) the absence of an intense Soret band and well-defined Q-bands and one order of reduction in the ε value, as observed in **3**,[20c] suggests the macrocycle reported here is not aromatic. Overall, the electronic absorption spectrum of **4** reflects the absence of effective π-delocalization and the spectral profile is similar to **2**. Upon protonation of **4** with dilute solution of TFA in CH_2Cl_2, the color of the solution changed from blue to green. The intense band and weak absorption bands are further red-shifted by 4 nm and 86, 121 nm and observed at 371 and 698, 765 nm, respectively, where the intensity of the higher energy band is reduced as compared to **4** (Supporting Information, Figures S7, S8).

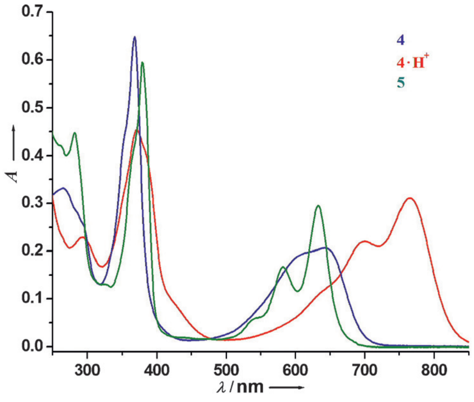

Figure 1. The electronic absorption spectrum of **4**, **4**·H^+, and **5**.

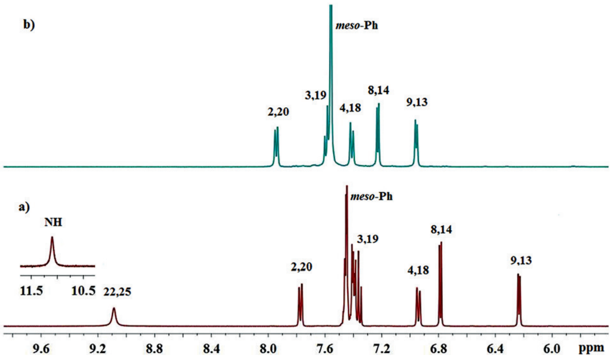

Figure 2. ^1H NMR spectrum of a) **4** and b) **5** in CD_2Cl_2.

The ^1H NMR spectrum of **4** was recorded in CD_2Cl_2 and shown in Figure 2a. There are four doublets in the deshielded region between 6.23 to 7.77 ppm, where the initial two doublets at 6.23 (H9,13) and 6.79 ppm (H8,14) are assigned to the two pyrrolic β-CH protons. The other two doublets at 6.94 (H4,18) and 7.77 ppm (H2,20) correspond to the biphenyl CH protons that are on the periphery, where the remaining outer biphenyl CH (H3,19) proton appears as a triplet at 7.36 ppm. The inner core biphenyl CH (H22,25) is a singlet at 9.09 ppm, while the pyrrolic NH (H24) signal is appeared as a broad singlet at 11.15 ppm, respectively. This was further confirmed by 2D homonuclear correlation spectroscopy (COSY) (Supporting Information, Figure S17). The presence of NH is further confirmed by CD_2Cl_2/D_2O exchange experiment. The *meso*-phenyl protons are found as a multiplet between 7.38 and 7.48 ppm. The chemical shift difference between the pyrrolic inner NH and outer β-CH protons ($\Delta\delta$) and the biphenyl inner CH and outer CH ($\Delta\delta'$) in **4** is 4.64 and 2.15 ppm. Overall, the spectral features and the chemical shift difference clearly reflect the nonaromatic features of **4**. The results are further compared with **2**,[4b] **3**,[20c] and phenanthriporphyrin,[19] where the $\Delta\delta$ values are 3.55, 11.84, and 11.86 ppm; on the other hand, the $\Delta\delta'$ values in **2**[4b] and phenanthriporphyrin[19] are 0.4 and 10.76 ppm, respectively. The shift difference ($\Delta\delta$ and $\Delta\delta'$) is comparable with **2** further confirms the nonaromatic character in **4**. Upon protonation of **4** with TFA in CD_2Cl_2, the biphenyl inner-CH (H22,25) and pyrrolic NH (H23,24) with integration of two protons are shielded by 0.69 and 1.53 ppm and observed at 8.40 and 9.62 ppm, respectively, however, the outer core biphenyl CH and pyrrolic β-CH signals are slightly deshielded (Supporting Information, Figure S21). The $\Delta\delta$ and $\Delta\delta'$ values are 2.67 and 1.17 ppm, thus indicating no macrocyclic aromatic ring current in the protonated state.[4e]

The final confirmation came from the single-crystal X-ray structure determination of **4** (Supporting Information, Table S5). The crystals were grown in a CH_2Cl_2/*n*-hexane solvent mixture. The unit cell contains two molecules of **4** (A and B; Supporting Information, Figure S28c) and one (A) of the two crystallographically independent molecules is shown in Figure 3a. As predicted from the spectroscopic analysis, the macrocycle contains a biphenyl, *meso*-pentafluorodipyrromethene units and are connected by two *meso*-phenyl units. The crystal analysis reveals that the weak intramolecular hydrogen bonding interactions between one of the inner-core biphenyl CHs (C6−H6), pyrrolic NH (N1−H1) with pyrrolic imine nitrogen (N2) with a bond distance and angle of 2.26 Å, 123° (N1−H1···N2) and 2.33 Å, 124° (C6−H6···N2), reflects the observed deshielding signals of inner NH and biphenyl CH protons from the NMR spectral analysis. The bond lengths of C5−C7, C1−C35, and C11−C13 are 1.478 Å, 1.468 Å, and 1.473 Å (Supporting Information, Figure S31), reflecting that the two *m*-benzene rings in the biphenyl unit and also the dipyrromethene and biphenyl units are connected by sp^2–sp^2 single-bond character.[4b,19] The carbon–carbon bond lengths within the biphenyl unit are between 1.366 and 1.408 Å, which have sp^2–sp^2 double-bond character and an average angle of 119.963° (Supporting Information, Figures S31, S32, Tables S1, S2), confirming that the biphenyl unit maintains the individual aromatic character as such.[27] The alternative sp^2–sp^2 single- and double-bond character between 1.469 and 1.325 Å in the dipyrromethene moiety predicts the effective π-delocalization within the unit (Supporting Information, Figures S31, S32).[19] Overall, the π-electrons present in the biphenyl unit did not participate in the macrocyclic aromatization, and thus remain isolated from the π-electron delocalization of the dipyrromethene unit. Thus, the absence of diatropic ring current as observed from the NMR spectral studies, further confirms the overall nonaromatic character from the crystal analysis. The pyrrole units in **4** are hardly deviated from the mean plane (contains the core atoms C6-C12-N1-N2) with the maximum deviation of 2.93°, whereas the *m*-benzene rings in the biphenyl unit are deviated by 19.52° and 20.06° which are located above and below the plane (Figure 3b). Both the molecules in the unit cell (A and B) are connected individually and combined together to generate series of 1D arrays, self-assembled dimers, and tetrameric structures (Supporting Information, Figures S29, S30).

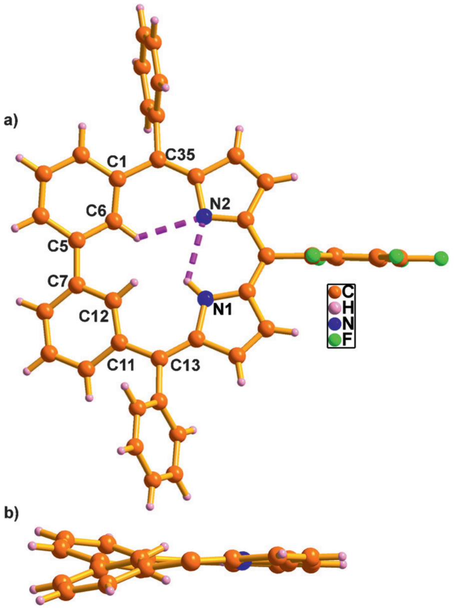

Figure 3. Single-crystal X-ray structure determination of **4**.[30] a) Top view and b) side view. The *meso* aryl groups are omitted for clarity in the side view.

The presence of two inner-core biphenyl CHs and pyrrolic NH prompted us to carry out metal ion insertion. The coordination chemistry of **4** was performed by using Cu^{II} salts. When **4** was treated with $Cu(OAc)_2$ in CH_2Cl_2/CH_3OH mixture, the blue fraction was eluted by neutral alumina column, affording **5** in 90% yield (Scheme 1). The ESI-MS spectral analysis of **5** in the solid state showed a molecular ion peak at 699.0691 [M+1] (Supporting Information, Figure S5), confirming the exact composition. The electronic absorption spectrum showed an intense band at 380 nm, which was red-shifted by 13 nm compared to **4**, while the weak bands were blue-shifted by 27 and 9 nm and observed at 585 and 635 nm, respectively (Figure 1). The ^1H NMR spectrum was recorded in CD_2Cl_2 and shown in Figure 2b. The pyrrolic β-CHs are resonated as two doublets at 6.96 (H9,13) and 7.23 (H8,14); on the other hand, the outer-core biphenyl CHs are observed at 7.41 (H4,18), 7.60 (H3,19), and 7.94 ppm (H2,20), respectively. This was further confirmed by ^1H–^1H COSY spectral analysis (Supporting Information, Figure S20). The slightly deshielded pyrrolic β-CH and outer-core biphenyl CHs and the disappearance of inner-core biphenyl CHs and pyrrolic NH signals as compared to **4** confirms the formation of diamagnetic organometallic Cu^{III} complex **5** and also maintains the nonaromatic character as such upon metal ion insertion. It is pertinent to point out that the reaction of **2** with $CuCl_2$ forms internal carbon chlorinated mixed-valence (Cu^I and Cu^{II}) tetranuclear copper complex.[4c] On the other hand, **3** reacts with $Cu(OAc)_2$ to form a higher-oxidation-state Cu^{III} complex at room temperature.[20b,d]

The explicit structure of organo-Cu^{III} complex of **5** was unambiguously confirmed by single-crystal X-ray diffraction analysis (Supporting Information, Table S5). A suitable single crystal was grown by slow diffusion of *n*-hexane vapors over CH_2Cl_2 solution of **5** and the structure is shown in Figure 4a. As predicted from the spectral analysis, the Cu^{III} ion is inserted inside the macrocyclic framework and the geometry around the metal center is square planar with N1-Cu-N2, N2-Cu-C6, C6-Cu-C12, and C12-Cu-N1 angles of 93.175°, 91.170°, 82.706°, and 92.208°, and the Cu−C6, Cu−C12, Cu−N2, and Cu−N1 bond lengths are 1.946 Å; 1,953 Å; 1.918 Å, and 1.907 Å, respectively (Supporting Information, Figure S36, Table S3). As compared to Cu−C and Cu−N bond lengths of organo-Cu^{III} complexes of *cis*-[14a] and *trans*-

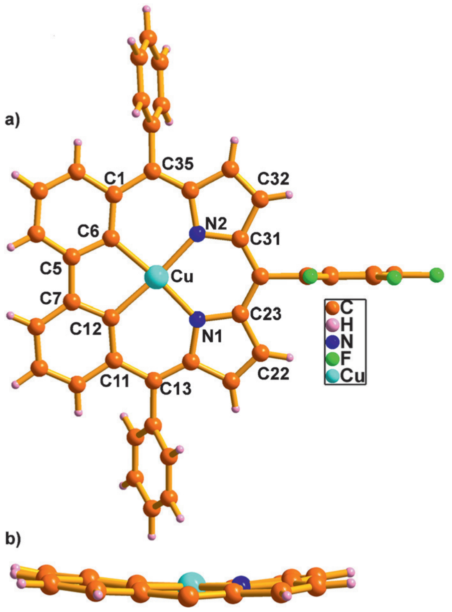

Figure 4. Single-crystal X-ray structure of **5**.[30] a) Top view and b) side view. The *meso* aryl groups are omitted for clarity in the side view.

doubly[14b] N-confused porphyrins, the Cu–C bond lengths of **5** are larger and Cu–N bond lengths are shorter;[14] however the latter bond lengths (Cu–N) are longer compared to $\mathrm{Cu^{III}}$ complexes of **3**.[20b,d] The biphenyl and the pyrrole units are deviated from the mean plane containing the core atoms (C6-C12-N1-N2-Cu) with the tilt angle between 6.49° and 8.97°, respectively (Figure 4b). As observed in **4**, the complex **5** retains the nonaromatic character, the results are reflected from the crystal analysis, where 1) the biphenyl and dipyrromethene moieties (bond lengths in C5–C7, C1–C35, and C11–C13 are 1.457 Å, 1.441 Å, and 1.463 Å) are connected by sp^2–sp^2 single-bond character; 2) there is individual aromatic character within the biphenyl unit (bond distances are between 1.364 and 1.418 Å and the average angle is 119.982°); and 3) there is an effective π-delocalization within the dipyrromethene unit (bond distances are between 1.328 and 1.450 Å; (Supporting Information, Figure S36, Table S3). The presence of fluorine atoms in the pentafluoro units generates series of intermolecular hydrogen bonding interaction to form a self-assembled dimer (Supporting Information, Figure S33c) and 1D arrays (Supporting Information, Figure S34). The dimer and arrays are combined together to generate a 2D supramolecular assembly in the solid state (Supporting Information, Figure S35).

The possible equilibrium between the diamagnetic $\mathrm{Cu^{III}}$ complex (**5**) and paramagnetic $\mathrm{Cu^{II}}$ radical cation was investigated and the results are summarized as follows: 1) The saddling dihedral angle value (χ_1–χ_4) in **5** is between 0.674° and 7.603° (Supporting Information, Table S4), which is less as compared to $\mathrm{Cu^{III}}$ complexes of **3**;[20b,d,28] 2) the variable-temperature NMR experiments of **5** showed a sharp signal at higher temperature, reflecting that the thermally accessible paramagnetic states are absent (Supporting Information, Figures S23, S24); and 3) the EPR experiments of **5** in solution and solid state at variable temperature are silent (Supporting Information, Figure S26, S27). Overall, the results confirmed the ability of **4** to stabilize the higher oxidation state $\mathrm{Cu^{III}}$ ion. Furthermore, the resolved diamagnetic spectrum of **5** in [D$_5$]pyridine (Supporting Information, Figure S25) confirms the absence of axial ligation and thus that a d^8 low-spin configuration is maintained.[29]

In conclusion, we have demonstrated the synthesis, spectroscopic, and structural characterization of 6,11,16-triarylbiphenylcorrole and its metal complex. The aromatic biphenyl unit and the π-delocalized dipyrromethene moiety were linked together to generate the overall nonaromatic character. The free ligand with contracted size and trianionic nature with *adj*-CCNN core was crucial for the formation of the organocopper complex with two M–C bond, which is diamagnetic and affords square-planar geometry around the metal center. The chemistry is now being extended to the pyridine-containing macrocycles and also the exploration of the possibilities of synthesizing respective aromatic corrole derivatives, which is currently underway in our research group.

Keywords: copper · dicarbacorrole · nonaromaticity · organometallic complexes · porphyrin

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[30] CCDC 1052113 (**4**) and 1051683 (**5**) contain the supplementary crystallographic data for this paper. These data are provided free of charge by The Cambridge Crystallographic Data Centre.

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