An Auxiliary Pyrrole Triggered Macrocycle Transformations from Norrole to Isonorrole and N-Confused Corrole with a Fused Hexacyclic Ring**

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Abstract: Three kinds of fused porphyrinoids, **L2–L4**, possessing different types of corrole-based frameworks were synthesized from a pyrrole-substituted corrole isomer (norrole **L1**). Oxidation of **L1** afforded a unique N-C_{meso}-fused pyrrolyl isonorrole **L2**, involving the fusion of auxiliary pyrrolic NH moiety with a meso-sp³-carbon. Subsequently, **L2** underwent macrocycle transformations to give singly and doubly N-C_{Ar}-fused N-confused corroles, **L3** and **L4**, respectively. Notably, **L3** and **L4** contain fused [5.7.6.5]-tetra- and [5.6.7.7.6.5]-hexacyclic structures, respectively, involving lateral annulation. These skeletal transformation reactions from norrole to its isomer, isonorrole, and finally to N-confused corrole indicate that multiply-fused porphyrinoids could be readily synthesized from the pyrrole-appended confused porphyrinoids.

Corrole is one of the most widely studied contracted tetrapyrrolic macrocycles containing four pyrrolic units interconnected at the α positions through three meso-carbon atoms in a (1.1.1.0) fashion (Figure 1).^[1] Unlike the parent porphyrin skeleton, such a contracted core structure gives rise to the hitherto promising potency as catalysts for oxidation due to the stabilization of high valent metals through a distinct smaller and trianionic

coordinating environment and as photo-sensitizers in light-driven conversion to electricity.^[2] Thus, it is of predominant importance to develop methodology for diverse functionalization of corroles for various applications.^[3] However, the direct skeletal modification of a corrole core and its functionalization still remains in infancy, since such analogs are usually less stable compared to the parent corrole and often exhibit unexpected reactivity.^[4]

Figure 1. Chemical structures of porphyrin, corrole, and their analogues.

In order to open the way for this issue, we envision that a “confusion approach”^[5] can systematically realize new electronic structures through varying the linking modes of pyrrolic subunits, e.g., C α -C β ,^[6] C β -C β ,^[7] or N-C α .^[6c, 8] (Figure 1). Among them, a representative class of neo-confused porphyrinoids possessing a particular pyrrolic unit linked with the N-C bond fashion affords electronically perturbed π -platforms with a polarized N-C covalent bond.^[8] Notably, they retain 18 π -conjugation circuits, and the corresponding properties such as extended absorption, tunable aromaticity, anion binding ability, cation complexation, and oxidative coupling reactivity of inner carbon have been thus demonstrated.^[9]

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On the other hand, oxidative fusion reaction is useful to create highly conjugated core skeletons such as electron rich π -conjugated compounds.^[4b, 10] Here, we are focused on the pyrrolyl norrole (**L1**, Scheme 1), whose unusual ring expansion reaction to pentaphyrin was shown previously.^[11] Taking advantage of regioselective reactivity of the α -pyrrolic CHs as well as the structural flexibility originated from the interpyrrolic N-C linkage of neo-confused corrole, auxiliary pyrrole appended at the adjacent α position of norrole is expected to trigger a fusion reaction through the weakly acidic pyrrole NH site.^[12] Thus, in this study, analysis of the oxidative fusion of norrole **L1** demonstrated the formation of N-*C_{meso}*-fused isocorrole isomer, **L2** (termed as an isonorrole, Scheme 1). Different from the regular isocorroles,^[13] the isonorrole **L2** can be regarded as a novel class of tetrapyrrolic macrocycle, which showed further reactivity for ring fusion reactions.^[14] The singly and doubly N-*C_{Ar}*-fused N-confused corroles (**L3** and **L4**, respectively) were subsequently generated accompanying with the double skeletal rearrangement of N-C linkages (i.e., N-*C_α* and N-*C_{meso}*). The core transformation from norrole to isonorrole, and finally to N-confused corrole can alter their photophysical and electrochemical properties due to the lateral annulation of an auxiliary pyrrole unit and the C₆F₅ moieties.

Scheme 1. Syntheses of **L2**–**L5**. Conditions: i) DDQ, CH₂Cl₂; ii) NBS, CH₂Cl₂; iii) toluene, reflux; iv) DMF, 30 °C. (R = COC₆F₅)

Details of the syntheses are outlined in Scheme 1. Treatment of **L1**^[11] with one equivalent of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) in CH₂Cl₂ yielded the isonorrole **L2** in a 63% yield by N-C fusion of the appended pyrrolic NH with the neighboring *meso*-carbon.^[15] Under this condition, the pentaphyrin **L5** reported earlier was formed as the second major product.^[11] Interestingly, **L2** undergoes a regioselective bromination reaction at one of the two free pyrrolic α positions to afford **L2-Br** in a yield of 66% upon addition of *N*-bromosuccinimide (NBS, 0.9 equiv). Considering the presence of an *sp*³ *meso*-carbon and a reactive interpyrrolic N-C linkage in the framework of **L2**, it is anticipated that **L2** may be susceptible to the ring opening or skeletal transformation if suitable conditions are applied. Consistent to this expectation, when a toluene solution of **L2** was refluxed for 10 h, a

skeletal rearrangement occurs with a concurrent fusion of the appended pyrrolic nitrogen with the C₆F₅ moiety. The pyrrolyl-fused N-confused corrole **L3** was obtained in an 8% yield accompanied with **L5** in a 32% yield. Since the N-confused corrole **L3** still contains a bare pyrrolic NH site located close to the C₆F₅ moiety, a further fusion could be expected.^[16] Thus, **L3** was stirred in DMF for 4 h at 30 °C to afford further fused corrole **L4** in an 88% yield. There is a sharp contrast that no reaction occurred when THF was used as a reaction media instead of DMF, which implies the basic solvent facilitates the reaction through deprotonation of the NH group of **L3**, followed by its nucleophilic attack at the C₆F₅ moiety. In fact, **L4** was not formed upon refluxing the toluene solution of isonorrole **L2**, which may be ascribed to the non-basic nature of the solvent. The structures of the products obtained in this study were characterized by various spectroscopies.

Combined with the structural analysis of **L2-Br** (*vide infra*), it is noted that **L2** is generated via oxidative dehydrogenation of **L1**. The ¹H NMR spectrum of **L2** in CDCl₃ shows only one NH signal at δ = 14.67 ppm (Figure S1), whereas three NH signals are present in **L1**. Disappearance of two NH protons is consistent with the observed oxidation triggered ring fusion reaction. The characteristic signal at δ = 68.3 ppm in the ¹³C NMR spectrum supports the isonorrole structure with an *sp*³ *meso*-carbon. Due to disruption of the conjugation in **L2**, the pyrrolic β -H signals lie in the range of 5.8–7.0 ppm, reflecting its nonaromatic character.

The X-ray crystal structure of brominated derivative, **L2-Br** gave more solid evidence for the intrinsic structure of isonorrole (Figures 2a,c).^[17] A [5.5.5]-tricyclic fused moiety formed by connection of the nitrogen atom of the appended pyrrole with the neighboring *meso*-carbon atom is present in **L2-Br**. The *meso*-carbon is arranged as an *sp*³ hybridized carbon with the typical tetrahedral angles of approximately 109.5°. The tripyrrin unit (namely, pyrrole rings A–C) is nearly coplanar involving the effective inner hydrogen bonds. The fused tricyclic unit (rings D–F) are lying approximately perpendicular to the tripyrrin with an interplanar angle of 72.1°, which is more severely distorted with respect to that of norrole (36.4°)^[6c] due to the presence of the *sp*³ *meso*-carbon. Based on the analogy of **L2-Br** and **L2** in the ¹H and ¹³C NMR spectra (Figures S1–S6), the distorted isonorrole-like structure was characterized.

Upon transformation from **L2** to **L3** and **L4**, the typical spectral features of N-confused corrole^[6c] emerged in the ¹H and ¹³C NMR spectra (*cf.* SI). The signal at δ = 13.20 ppm assigned as an outer NH appears in the lower field and two inner NH signals appear in a relatively high field at δ = 8.52 and 4.56 ppm in the ¹H NMR spectrum of **L3** (Figure S7). As well, one inner CH appears in the upper field at δ = 2.12 ppm. These features imply the recovery of aromaticity, although the strength is likely weak judging from the maximum difference between the chemical shifts of peripheral CH moieties and those of interior CH or NH moieties ($\Delta\delta_{\text{CH-CH}}$ = 5.6 ppm and $\Delta\delta_{\text{CH-NH}}$ = 3.2 ppm).^[6c, 18] Thus the skeletal rearrangement of isonorrole to the N-confused corrole derivative is anticipated.

Subsequently, the ¹H NMR spectrum of **L4** was essentially same as that of **L3** except for the loss of an outer NH signal (Figure S10). The observation of a loss of 20 mass numbers relative to **L3** in the mass spectroscopy allowed us to speculate the further fusion of the outer NH with the neighboring C₆F₅ moiety. The structural support for the fused N-confused corrole skeletons in **L3** and **L4** was given by the unambiguous X-ray crystallographic analysis of **L4** (Figures 2b,d).^[17] An N-confused corrole core skeleton was seen along with two N-fused ring systems involving the linkage of the confused and the appended pyrrolic moieties with the neighboring C₆F₅ groups. The resulting [5.6.7.7.6.5]-hexacyclic ring unit (rings: D–I) is highly distorted relative to the tripyrrin core unit (rings: A–C); the pyrrole ring D is tilted from the tripyrrin mean plane by an angle of 44.1° and interplanar angles for the rings D/E, D/F, and D/I are 36.3°, 43.4°, and 38.1°, respectively. The embedded seven-membered rings in the peripheral ring system may introduce a strained curvature as seen in the warped nanographene.^[19]

Figure 2. Complementary views of the molecular structures of **L2-Br** (a, c) and **L4** (b, d). C_6F_5 groups and hydrogen atoms attached to carbon are omitted for clarity. The dotted lines represent hydrogen bonds.

Figure 3. Relative energies for the possible isomers of **L3**. The arrow on **L3a** indicates the hydrogen bonding.

From the mechanistic viewpoint in the formation of doubly fused corrole analogue **L4**, the singly fused corrole **L3** can be regarded as an intermediate containing a fused [5.7.6.5]-tetracyclic ring with one of the pyrrolic NH moieties, either the N-confused or the appended one. To clarify the N- C_{Ar} bond formation occurring in **L3** in details, the relative energies of the plausible isomers and conformers of **L3** were examined by density functional theory (DFT) calculations (Figure 3). Owing to the proximity between the NH and the C_6F_5 moieties, among the isomers, the models, **L3a'** and **L3b** are subject to severe intramolecular steric hindrance. Instead, the geometry of **L3a** is energetically over 10 kcal mol⁻¹ more stable than the rest due to the effective hydrogen bonding between the outer NH and the carbonyl O atom as well as the lack of intramolecular steric hindrance. This agrees well with the experimental observation; the extraordinarily down field shift of the outer NH signal of **L3** was seen compared to that of the reported N-confused corrole (e.g., $\delta = 13.20$ ppm vs. 9.24 ppm, respectively).^[6c] Moreover, the chemical shift of outer NH for **L3** is insensitive to the solvent media (e.g., CDCl_3 -[D_6]DMSO) (Figure S13).^[20] These observations may be rationalized by the presence of a strong intramolecular hydrogen bond between the outer NH and the carbonyl O atom. Thus, the structure of **L3a** would be described as the most probable conformer (Figure 3). Upon deprotonation of the pyrrolic NH moiety in **L3**, the rotation barrier of the C_6F_5 ring may largely decrease to facilitate the formation of doubly fused product **L4**.

The absorption spectra of **L2-L4** exhibit two sets of broad bands with comparable intensities in the ranges of 340–380 nm and 460–750 nm, respectively (Figure 4). The nonaromatic isonorrole **L2** shows almost featureless spectra, whereas the fused N-confused corroles **L3** and **L4** exhibit clear vibronic structures in the Q-band regions, which is similar to the reported N-confused corrole.^[6c] The bathochromically shifted spectra of **L3** and **L4** relative to **L2** could be rationalized by the recovery of the conjugation framework in these two compounds. As well, the peripheral fusion allows the extension of the absorption band edges for approximately 50 nm relative to that of N-confused corrole.^[6c]

In an effort to gain the HOMO-LUMO energy insights for the corrole derivatives, redox potentials of **L2-Br** and **L2-L4** (Figure S20 and Table S1) were determined by cyclic voltammetry in CH_2Cl_2 containing 0.1 M tetra-*n*-butylammonium hexafluorophosphate. Isonorroles **L2** and **L2-Br** exhibit irreversible oxidation waves at 0.65 and 0.76 V (vs Fc/Fc^+) and facile reduction waves at -0.99 and -0.89 V, respectively, which result in the almost identical electrochemical HOMO-LUMO gaps of 1.64 and 1.65 V, respectively. Upon transformation to N-confused corroles, the first oxidation and the first reduction potentials are determined at 0.49, 0.55, -1.23, and -1.24 V, and thus the electrochemical HOMO-LUMO gaps are 1.72 and 1.79 eV for **L3** and **L4**, respectively. The HOMO-LUMO gaps of **L2-L4** estimated from DFT calculations are to be 1.95, 2.14, and 2.18 eV, respectively, with a tendency in agreement with that of the electrochemical data (Figure S21).

Figure 4. UV-vis spectra and photographs showing the solution colors of **L2-L4** in CH_2Cl_2 .

Notably, **L2** exhibits the smallest HOMO-LUMO gap among **L2-L4**, which seems to be inconsistent with the fact that the lowest energy peak for **L2** appears at 581 nm, a shorter wavelength relative to 620 and 612 nm for **L3** and **L4**, respectively. This inconsistency can be interpreted from further time-dependent DFT calculations, which indicates that the hypsochromic shift of **L2** arises from the noticeable admixture of the HOMO-1 $\rightarrow$ LUMO into the HOMO $\rightarrow$ LUMO transition, thus enlarging the corresponding excitation energy (Table S2). In contrast, the corresponding absorption bands for **L3** and **L4** almost involve pure HOMO $\rightarrow$ LUMO transitions.

In summary, using the unique reactivity of the norrole appended auxiliary pyrrole moiety, **L1**, we have synthesized three novel corrole isomers, **L2-L4**. Notably, the oxidative fusion reaction of **L1** afforded N- C_{meso} -fused pyrrolyl isonorrole **L2** where one of the *meso*-carbon atoms is sp^3 -hybridized. It was found that such species is highly reactive towards macrocycle transformation reactions. Consistently, isonorrole **L2** was converted into singly and doubly N- C_{Ar} -fused N-confused corroles, **L3** and **L4**. Unprecedented [5.7.6.5]-tetra- and [5.6.7.7.6.5]-hexacyclic fused ring structures involving lateral annulation were formed beside the macrocyclic cores. The “confusion approach” products shown here would bring forth interesting heteroacene architectures whose properties can be easily modulated by the metal coordination of the novel corrole-based macrocyclic units associated.

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Entry for the Table of Contents

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<p>M. Li, P. C. Wei, M. Ishida, X. Li, M. Savege, R. Guo, Z. P. Ou, S. H. Yang, H. Furuta*, and Y. S. Xie* _____</p> <p>Page – Page</p> <p>An Auxiliary Pyrrole Triggered Macrocycle Transformations from Norrole, to Isonorrole and N-Confused Corrole with a Fused Hexacyclic Ring</p>		<p>The pyrrole-substituted corrole isomer (norrole) underwent an oxidative fusion reaction to afford a unique N-<i>C_{meso}</i>-fused isonorrole, which was successively converted into singly and doubly N-<i>C_{Ar}</i>-fused N-confused corroles with unprecedented fused [5.7.6.5]-tetra- and [5.6.7.7.6.5]-hexacyclic structures, respectively, involving lateral annulation.</p>