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C-Fused Norrole: A Fused Corrole Isomer Bearing a N,C-Linked Bipyrrole Unit

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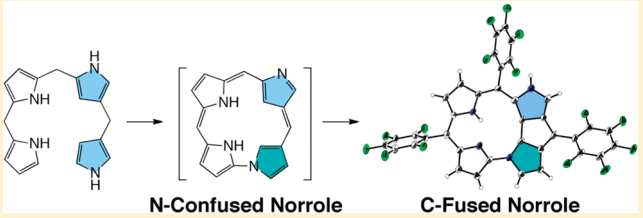
Supporting Information

ABSTRACT: Oxidative cyclization of a doubly N-confused bilane afforded a N-confused N,C-linked corrole (N-confused norrole), which was readily oxidized to form a C-fused N,C-linked corrole (C-fused norrole).



Corrole is a tetrapyrrolic macrocycle containing a direct C,C-linkage between two neighboring pyrrole rings.[1] Corrole has an ability to stabilize transition metal centers of high oxidation states due to its trianionic character and a narrow space of the macrocyclic core.[2] Recent studies revealed that corrole derivatives would be promising candidates as catalysts and biologically active substances.[3] Thus, studies on corrole and related compounds have become one of the most active research fields in the porphyrinoid chemistry.[4]

Recently, we have reported a series of corrole (COR) isomers, namely, N-confused corrole (NCC) and N,C-linked corrole or norrole (NOR).[5] The latter was the first example of oligopyrrolic macrocycles possessing a N,C-linked bipyrrole moiety in their skeletons. The finding of this unusual N,C-linkage inspired us to explore a scope of N,C-linked oligopyrrolic macrocycles. Consequently, we have designed a new member of the corrole family, N-confused norrole (NCN, Figure 1), which is also a member of multiply N-confused tetrapyrrolic macrocycles.[6]

For the stepwise synthesis of a series of multiply N-confused porphyrinoids, it is necessary to handle the multiply N-confused oligopyrroles as precursors or key building blocks, freely. However, in spite of recent development in the synthesis of N-confused porphyrinoids,[7] poor examples have been reported for the syntheses of such oligopyrroles.[8] Hence, a rapid and convenient method for the synthesis of multiply N-confused oligopyrroles was investigated in advance.

First, preparation of doubly N-confused dipyrromethane (**2**) was examined by acid-catalyzed condensation reactions of 1-(triisopropylsilyl)pyrrole (TIPS-pyrrole, **1**) as shown in Table 1. The TIPS group effectively disturbs the reaction at α-pyrrolic positions due to steric hindrance.[9] Upon treatment of **1** (10 equiv) and C_6F_5CHO (1 equiv) with trifluoroacetic acid (TFA, 0.5 equiv), the desired product (**2**) was obtained in 19% yield (entry 1). Disappointingly, singly N-confused dipyrromethane (**3**) was also obtained as a major product in 29% yield. This

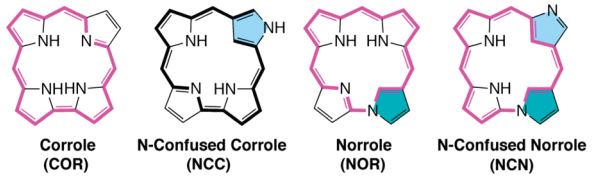


Figure 1. Structures of the corrole isomers.

undesired product ratio was not improved by decreasing the amount of TFA (entry 2). Meanwhile, usage of BF_3•OEt_2 resulted in considerable refinement of product selectivity to give **2** in 27% yield together with **3** in 13% yield (entry 3). Further improvement was attained by adding CH_2Cl_2 as solvent, and the yield of **2** reached up to 46% (entries 4−6). While we suspect an acid-catalyzed conversion from **2** to **3**, such isomerization was not yet observed by treatment of **2** with acids.

Second, doubly N-confused bilanes (linear tetrapyrroles) were synthesized (Scheme 1). Deprotection of **2** with $Bu_4N^+F^-$ proceeded quantitatively to give **4**. Then, acylation reaction of **4** was achieved with a thioester method[10] to give acylated products **5** and **6** in 42 and 15% yields, respectively. The attempts of acylation with pentafluorobenzoyl chloride resulted in the lower yields. Reduction of **5** with excess $NaBH_4$ and subsequent TFA-catalyzed condensation reaction with dipyrromethane gave doubly N-confused bilane **8** in 44% yield (two steps). Similarly, reduction of **6** and subsequent condensation reaction with pyrrole gave **10**, an isomer of **8**, in 84% yield.

Finally, oxidative intramolecular cyclization reactions of doubly N-confused bilanes were investigated. When **8** was treated with a variety of oxidants, such as 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ), *p*-chloranil, *o*-chloranil, or $FeCl_3$,

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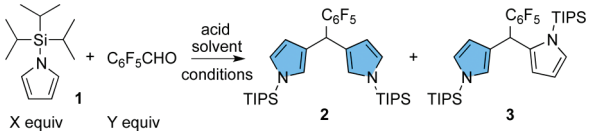
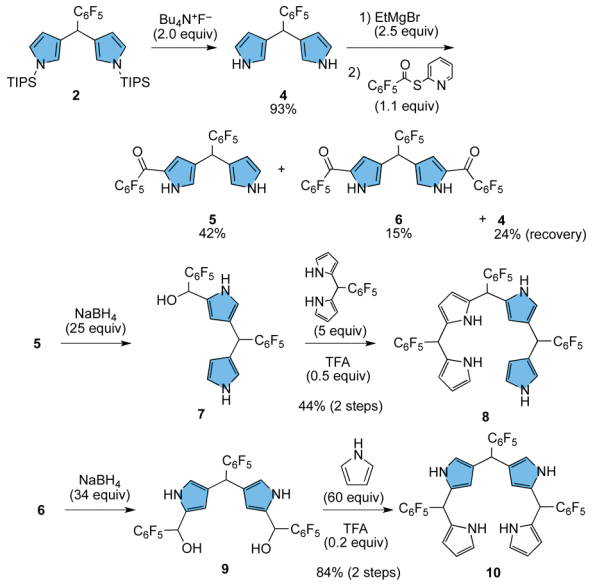
Table 1. Acid-Catalyzed Condensation Reactions of TIPS-Pyrrole and Pentafluorobenzaldehyde



entry	*X*	*Y*	solvent	acid	conditions	yield of **2** (%)	yield of **3** (%)
1	10	1	none	TFA (0.5 equiv)	23 °C, 3 h	19	29
2	5	1	none	TFA (0.02 equiv)	23 °C, 33 h	13	18
3	5	1	none	$BF_3{\bullet}OEt_2$ (0.1 equiv)	0 °C, 105 min	27	13
4	5	1	CH_2Cl_2	$BF_3{\bullet}OEt_2$ (0.4 equiv)	0 °C, 30 min	42	23
5	2.5	1	CH_2Cl_2	$BF_3{\bullet}OEt_2$ (0.4 equiv)	0 °C, 10 min	24	19
6	5	1	CH_2Cl_2	$BF_3{\bullet}OEt_2$ (2 equiv)	0 °C, 5 min	46	6

Scheme 1. Preparation of Doubly N-Confused Bilanes



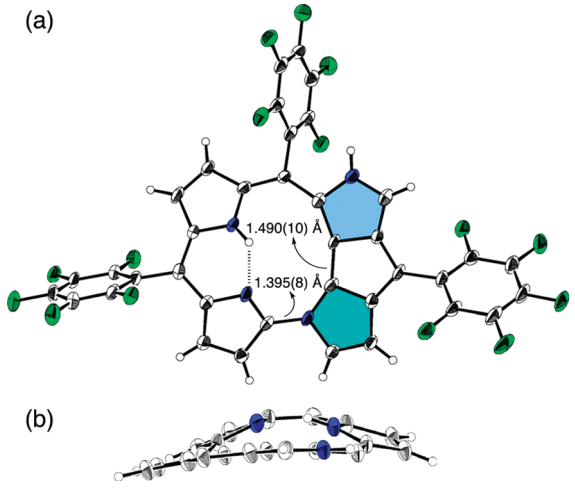


Figure 2. X-ray structures of **12**: (a) top view, (b) side view. The thermal ellipsoids are shown at the 30% probability level. The *meso*-aryl groups are omitted in (b) for clarity.

dehydrogenation reaction proceeded and analyses of the reaction mixtures by matrix-assisted laser desorption ionization mass spectra afforded an intense molecular ion peak of m/z = 796, which corresponds exactly to N-confused norrole (**11**) or doubly N-confused corrole (**13**). However, unfortunately, the corresponding product was readily oxidized or decomposed during purification, and isolation of **11** or **13** was so far unsuccessful. Since a weak peak of m/z = 794 was detected in many cases, more harsh conditions were applied. Thus, the reaction of **8** with DDQ in CH_3CN under reflux was achieved, and mass analysis of the crude product gave a strong molecular ion peak of m/z = 794. After silica gel column separation, C-fused norrole (**12**) was isolated in 2% yield as an air-stable solid. An intramolecular C,C-coupling reaction could be facilitated by the narrow space inside the macrocycle of **11** as well as high flexibility of the N-linked and N-confused pyrrole rings.[11] The reason for the low yield was partly explained by the competitive intermolecular oxidative coupling reactions leading to octapyrrolic and higher oligopyrrolic compounds, as judged by the mass analyses. Separately, oxidative cyclization reaction of **10** was also attempted with a variety of oxidants. However, no cyclic compound such as **14** was obtained, contrary to our expectation.

The structure of **12** was unambiguously determined by the X-ray crystallographic analysis. The ORTEP drawings of **12** are shown in Figure 2. Formation of the C−C bond inside the corrole macrocycle was evidently confirmed. Existence of the peripheral NH proton in the solid state was supported by formation of hydrogen bonding with CH_3CN in the crystal, where the N−N distance is 3.003 Å (Figure S9 in Supporting Information). Beside this, **12** showed an anion binding affinity for halide in CH_2Cl_2 solution (K_a = 80 M^{-1} for Cl^-), indicating the existence of a peripheral NH moiety even in solution. The C−C and C−N bond lengths newly formed by the oxidation reaction are 1.490(10) and 1.395(8) Å, respectively. Because of the narrow space inside the macrocycle, the dipyrromethene unit was distorted and deviated from planarity (Figure 2b).

Absorption spectrum of **12** in CH_2Cl_2 is shown in Figure 3. The split Soret-like bands were observed at 404 and 430 nm, and the Q-type band was observed at 606 nm. The theoretical oscillator strengths calculated with a time-dependent density functional theory (TDDFT) method are in good agreement with the experimental result.[12] In fluorescence measurement, very

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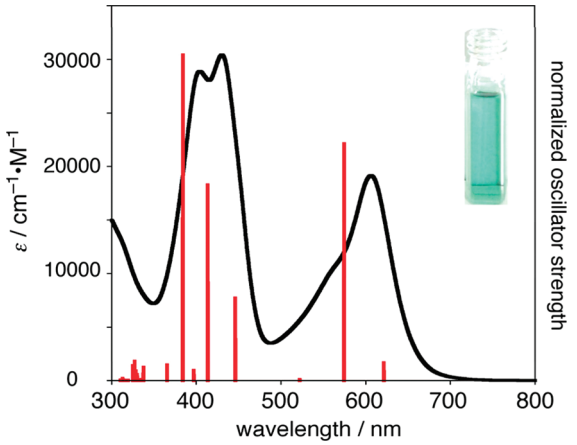


Figure 3. Absorption spectrum of **12** in CH_2Cl_2. Normalized theoretical oscillator strengths and solution color are also shown.

weak emission was observed at 679 nm in CH_2Cl_2 (Figure S10 in Supporting Information, $\Phi < 0.001$). The fairly large Stokes shift (1774 cm^{-1}) in **12** despite its rigid planar structure is uncommon among porphyrinoids, which can be rationalized by an intramolecular charge transfer process or structural transformation at the excited state. Because the solvent effect on UV−vis absorption of **12** is negligible (Figure S11 in Supporting Information), the intramolecular charge transfer process should be less important in its decay process. Thus, the large Stokes shift of **12** might be due to structural transformation at the excited state. Considering the rigid molecular skeleton of **12**, one of the plausible structural transformations at the excited state would be intramolecular proton transfer, which was also proposed for the rigid porphyrinoids like N-fused porphyrins.[13] Although no direct evidence was obtained yet, the ^{1}H NMR spectrum supported an excited state intramolecular proton transfer process in **12**. The NH signal inside the macrocycle was observed at δ 10.04 ppm in $CDCl_3$. The large low-field shift in spite of its aromatic character (vide infra) suggests the existence of strong intramolecular hydrogen bonding inside the macrocycle in the ground state, which would be an important factor for rapid intramolecular proton transfer.

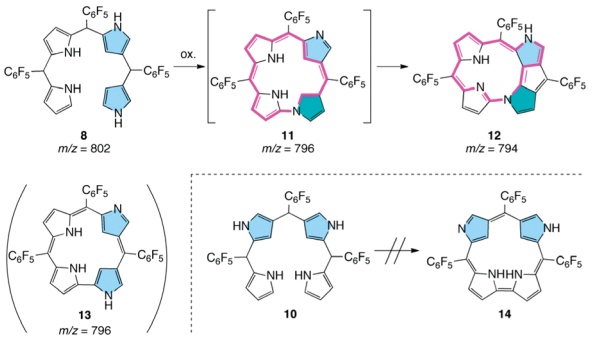
Aromaticity of **12** is evaluated experimentally as well as theoretically.[12] Theoretical study on a series of corrole isomers is achieved at the B3LYP/6-311++G**//B3LYP/6-31G** level on the *meso*-pentafluorophenyl derivatives in all cases. The mean difference in the bond lengths of main framework between the X-ray structure and the optimized structure of **12** is 0.013 Å, which supports reliability of the calculation method used. The ^{1}H NMR signals (in $CDCl_3$) of the pyrrolic CH moieties appear in the region from δ 7.1 to 8.4 ppm, which illustrates the existence of significant aromatic ring current. The nucleus independent chemical shift (NICS)[14] value for the optimized structure of **12** is −10.92 ppm (Table 2), indicating moderate or strong aromaticity of **12**. This value is smaller than that of COR (−12.14) but larger than that of NCC (−6.82) and NOR (−7.28). The HOMO−LUMO band gap energies (ΔE_{HL}) show a good correlation with the NICS values in these four compounds. In the case of NCN, the presumable precursor of **12**, the NICS value indicates nearly non-aromatic character (−2.91), possibly due to severe distortion from planarity imposed by four hydrogen atoms inside the macrocycle. Thus, the intramolecular C−C bond formation from NCN to **12** would be beneficial for aromatic stabilization through planarization. The harmonic

Table 2. NICS Values, HOMA Indices, and HOMO−LUMO Gap Energies of the Corrole Family

structure	NICS (ppm)	$HOMA_{all}$	$HOMA_{18}$	ΔE_{HL} (eV)
12	−10.92	0.471	0.537	2.29
COR[a]	−12.14	0.726	0.789	2.53
NCC[a]	−6.82	0.646	0.645	1.85
NOR[a]	−7.28	0.669	0.711	2.23
NCN	−2.91	0.571	0.632	2.00

[a] From ref 5.

Scheme 2. Oxidative Cyclization Reaction of 8



oscillator model of aromaticity (HOMA)[15] indices is also evaluated for the whole skeletons ($HOMA_{all}$) and [18]annulenic circuits ($HOMA_{18}$). The [18]annulenic circuits adopted are described by the colored bold lines in Figure 1 and Scheme 2. The black bold lines mean an absence of complete [18]annulenic circuits. Nevertheless, they were used for calculation of $HOMA_{18}$. The $HOMA_{all}$ index of **12** (0.471) is significantly smaller than those of COR (0.726), NCC (0.646), and NOR (0.669) in spite of its largely negative NICS value. It is even smaller than that of NCN (0.571). It could be rationalized by severe ring strain caused by the C−C fusion. Additionally, no significant differences are observed between $HOMA_{all}$ and $HOMA_{18}$. Hence, it would be difficult to explain the aromaticity of highly modified corrole analogues by analogy of simple [18]annulenic macrocycles or classical Kekulé description.

In conclusion, the method for the synthesis of doubly N-confused oligopyrroles was developed, and their oxidation reactions were examined. C-fused norrole (**12**) was isolated, and its considerable aromaticity was confirmed by the ^{1}H NMR measurements, which is a peculiar example of C-fused oligopyrrolic macrocycles. As the fusion reactions inside the macrocycles often afford the molecules of unique electronic structures, further development of this strategy is expected.[16] In addition, development on the porphyrinoids chemistry derived from the doubly N-confused oligopyrrole units is also expected.

EXPERIMENTAL SECTION

General. All of the reactions were performed in oven-dried reaction vessels under Ar or N_2. Commercially available solvents and reagents were used without further purification unless otherwise mentioned. CH_2Cl_2 was distilled over CaH_2. Dry THF (stabilizer free) was used as received. Thin-layer chromatography (TLC) was carried out on aluminum sheets coated with silica gel 60 F_{254}. Preparative separation was

performed by silica gel flash column chromatography (spherical, neutral, 40−50 μm) or silica gel gravity column chromatography (spherical, neutral, 63−210 μm). ^{1}H NMR spectra were recorded in $CDCl_3$ solution on a FT-NMR spectrometer at 300 MHz, and chemical shifts were reported relative to a residual proton of a deutrated solvent, $CHCl_3$ (δ = 7.26) in parts per million. ^{13}C NMR spectra were recorded in $CDCl_3$ solution on the same instrument at 75 MHz, and chemical shifts were reported relative to $CDCl_3$ (δ = 77.0) in parts per million. UV/vis absorption spectra were recorded on a UV spectrometer with a photomultiplier tube detector (190−750 nm) and a PbS detector (750−3200 nm). Emission spectra were recorded on a FL spectrometer with a photomultiplier tube detector (~850 nm). Mass spectra were recorded on a MALDI−TOF MS spectrometer. High-resolution mass spectra were measured with an ESI MS spectrometer.

5-Pentafluorophenyl-1,9-bis(triisopropylsilyl)-1,9-diaza-10,11-dicarbadipyrromethane (2) and 5-Pentafluorophenyl-1,11-bis(triisopropylsilyl)-1-aza-10-carbadipyrromethane (3). TIPS-pyrrole (1, 15.0 g, 67.1 mmol, 5.0 equiv) and pentafluorobenzaldehyde (1.66 mL, 13.4 mmol, 1.0 equiv) in 9 mL of dry CH_2Cl_2 were stirred at 0 °C under Ar for 10 min. Then, BF_3•Et_2O (3.36 mL, 26.8 mmol, 2 equiv) was added at 0 °C and stirred further for 5 min. The resulting reaction mixture was passed through a pad of alumina with CH_2Cl_2 as eluent and evaporated in vacuo. The residue was purified by silica gel column chromatography with hexane as eluent. The first fraction (R_f = 0.60; eluent, hexane) afforded recovered TIPS-pyrrole as a clear oil. The second fraction afforded **3** as a clear oil (523 mg, 0.873 mmol, 6.2%). The third fraction gave **2** as a clear white solid (3.85 g, 6.15 mmol, 45.8%). **2**: ^{1}H NMR ($CDCl_3$, 300 MHz, ppm) δ 1.06 (d, J = 7.5 Hz, 36H), 1.38 (sept, J = 7.5 Hz, 6H), 5.67 (s, 1H), 6.12 (br s, 2H), 6.57 (br s, 2H), 6.69 (br t, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz, ppm) δ 11.6, 17.7, 31.9, 110.5, 120.3*, 122.5, 124.0, 126.2, 137.5* (d, $^1J_{CF}$ = 249.1 Hz), 139.4* (d, $^1J_{CF}$ = 244.1 Hz), 145.0* (d, $^1J_{CF}$ = 246.6 Hz) (*these signals show a further multiplet coupling due to the remote ^{13}C−^{19}F coupling). Anal. Calcd for $C_{33}H_{50}F_5N_2Si_2$: C, 63.42; H, 7.90; N, 4.48. Found: C, 63.27; H, 7.85; N, 4.46; R_f = 0.30 (hexane). **3**: ^{1}H NMR ($CDCl_3$, 300 MHz, ppm) δ 1.01−1.07 (m, 36H), 1.27−1.50 (m, 6H), 5.71 (s, 1H), 5.98 (br, 1H), 6.22 (t, J = 3.0 Hz, 1H), 6.30 (br s, 1H), 6.33 (br s, 1H), 6.62 (t, J = 3.0 Hz, 1H), 6.79 (br s, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz, ppm) δ 11.6, 13.6, 17.7, 18.3, 34.2, 109.5, 110.6, 112.7, 122.8, 124.0, 125.5, 126.2, 136.1 (the signals due to the pentafluorophenyl moiety could not be assigned because of the complicated multiple coupling of ^{13}C−^{19}F); HRMS (ESI$^+$) found m/z 625.34110, calcd for $C_{33}H_{50}F_5N_2Si_2$ ($[M+H]^+$) m/z 625.34327; R_f = 0.45 (hexane).

5-Pentafluorophenyl-1,9-diaza-10,11-dicarbadipyrromethane (4). To a solution of **2** (360 mg, 0.576 mmol, 1.0 equiv) in 6 mL of THF was added $Bu_4^+NF^-$ (1 M in THF, 1.15 mL, 1.15 mmol, 2.0 equiv) at ambient temperature under Ar. After stirring for 90 min, the reaction was quenched by adding water and extracted with CH_2Cl_2. The combined organic layer was washed with water, dried over Na_2SO_4, and evaporated in vacuo. The residue was purified by silica gel column chromatography using hexane/CH_2Cl_2 = 4/1 (v/v) as eluent. The first fraction gave **4** as a clear oil (167 mg, 0.535 mmol, 93%): ^{1}H NMR ($CDCl_3$, 300 MHz, ppm) δ 5.79 (s, 1H), 6.26 (br s, 2H), 6.70 (br s, 2H), 6.74−6.77 (m, 2H), 8.03 (br s, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz, ppm) δ 31.7, 108.3, 116.2, 117.9, 119.8*, 123.9, 137.5* (d, $^1J_{CF}$ = 249.8 Hz), 139.5* (d, $^1J_{CF}$ = 249.1 Hz), 144.8* (d, $^1J_{CF}$ = 243.5 Hz) (*these signals show the further multiplet coupling due to the remote ^{13}C−^{19}F coupling.). Anal. Calcd for $C_{15}H_9F_5N_2$: C, 57.70; H, 2.91; N, 8.97. Found: C, 57.97; H, 2.89; N, 9.01; R_f = 0.50 (CH^2Cl_2).

2-Pentafluorobenzoyl-5-pentafluropheny-1,9-diaza-10,11-dicarbadipyrromethane (5) and 2,8-Bis(pentafluorobenzoyl)-5-pentafluropheny-1,9-diaza-10,11-dicarbadipyrro-methane (6). A THF solution of EtMgBr (3.34 mL, 3.34 mmol, 1.0 M, 2.5 equiv) was added to a stirred solution of **4** (417 mg, 1.34 mmol, 1.0 equiv) in THF (1.40 mL) under Ar. The mixture was stirred at ambient temperature for 10 min and then cooled to −78 °C. A solution of (*S*)-2-pyridyl pentafluorobenzothioate (448 mg, 1.47 mmol, 1.1 equiv) in THF (1.4 mL) was then added dropwise over 10 min. The solution was maintained at −78 °C for 7 min. The mixture was allowed to warm to room temperature. After 2.5 h, the reaction was quenched with saturated aqueous NH_4Cl. The reaction mixture partitioned between CH_2Cl_2 and water. Then, the CH_2Cl_2 phase was washed with water, dried over sodium sulfate, and evaporated in vacuo. The residue was separated by silica gel column chromatography, using hexane/CH_2Cl_2 = 1/4 (v/v) as eluent. The first fraction gave **4** as a clear oil (99.0 mg, 0.317 mmol, 24%). The second fraction gave **5** as a white solid (281 mg, 0.555 mmol, 42%). The third fraction gave **6** as a white solid (144 mg, 0.206 mmol, 15%). **5**: ^{1}H NMR ($CDCl_3$, 300 MHz, ppm) δ 5.63 (s, 1H), 6.12 (br s, 1H), 6.57 (br s, 1H), 6.62 (br s, 1H), 6.76−6.77 (m, 1H), 7.10 (br s, 1H), 8.14 (br s, 1H), 9.47 (br s, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz, ppm) δ 30.9, 107.8, 115.7, 118.1, 119.9, 122.1, 126.8, 127.8, 130.9, 172.2 (the signals due to the pentafluorophenyl moiety could not be assigned due to complicated multiple coupling of ^{13}C−^{19}F); HRMS (ESI$^-$) found m/z 505.04025, calcd for $C_{22}H_7F_{10}N_2O$ ($[M-H]^-$) m/z 505.03987; R_f = 0.30 (CH^2Cl_2). **6**: ^{1}H NMR ($CDCl_3$, 300 MHz, ppm) δ 5.61 (s, 2H), 6.54 (br s, 2H), 7.05 (br s, 2H), 9.59 (br s, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz, ppm) δ 31.0, 120.4, 126.6, 127.1, 131.6, 173.0 (the signals due to the pentafluorophenyl moiety could not be assigned because of the complicated multiple coupling of ^{13}C−^{19}F); HRMS (ESI$^-$) found m/z 699.01690, calcd for $C_{29}H_6F_{15}N_2O_2$ ($[M-H]^-$) m/z 699.01898; R_f = 0.15 (CH_2Cl_2).

5,10,15-Tris(pentafluorophenyl)-1,8-diaza-21,22-dicarbabilane (8). $NaBH_4$ (1.69 g, 44.8 mmol, 25 equiv) was added to a stirred solution of **5** (905 mg, 1.79 mmol, 1 equiv) in THF (100 mL) and MeOH (20 mL) at room temperature under N_2. After 1.5 h, the reaction was quenched with water and diluted with CH_2Cl_2. Then, the organic phase was washed with water, dried over Na_2SO_4, and evaporated in vacuo. The resulting product (**7**) was used in the next step without further purification. TFA (55.0 μL, 0.716 mmol, 0.5 equiv) was added to a solution of **7** and 5-pentafluorophenyldipyrromethane (2.80 g, 8.95 mmol, 5 equiv) in CH_2Cl_2 (20 mL) at room temperature under N_2. After stirring for 1 h, the reaction was quenched with water. The organic phase was washed with water, dried over Na_2SO_4, and evaporated in vacuo. The residue was purified by silica gel column chromatography using hexane/CH_2Cl_2 = 1/1 (v/v) as eluent. The first fraction (R_f = 0.30, hexane/CH_2Cl_2 = 2/3 (v/v)) afforded 5-pentafluorophenyldipyrromethane. The second fraction afforded **8** as a brown solid (957 mg, 1.19 mmol, 66.6%): ^{1}H NMR ($CDCl_3$, 300 MHz, ppm) δ 5.63 (s, 1H), 5.79 (br s, 1H), 5.86 (br s, 1H), 5.94 (br s, 3H), 6.02 (br s, 1H), 6.16−6.18 (m, 2H), 6.58 (br s, 1H), 6.62 (br s, 1H), 6.73 (br s, 1H), 6.74 (br s, 1H), 7.97 (br s, 1H), 8.07 (br s, 2H), 8.15 (br s, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz, ppm) δ 31.7, 33.08, 33.12, 33.15, 107.6, 107.77, 107.84, 107.87, 108.3, 108.6, 116.2, 116.4, 116.5, 118.0, 118.1, 123.6, 123.7, 124.6, 127.7, 127.9, 128.55, 128.63 (the signals due to the pentafluorophenyl moieties could not be assigned because of the complicated multiple coupling of ^{13}C−^{19}F). Anal. Calcd for $C_{37}H_{17}F_{15}N_4$: C, 55.37; H, 2.14; N, 6.98. Found: C, 55.58; H, 2.11; N, 6.94; R_f = 0.50 (hexane/CH_2Cl_2 = 1/4 (v/v)).

5, 10, 15-Tris(pentafluorophenyl)-7,13-diaza-22,23-dicarbabilane (10). $NaBH_4$ (276 mg, 7.30 mmol, 34 equiv) was added to a stirred solution of **6** (150 mg, 0.215 mmol, 1 equiv) in THF (16 mL) and MeOH (6 mL) at room temperature under N_2. After 3 h, the reaction was quenched with water and diluted with CH_2Cl_2. Then, the organic phase was washed with water, dried over Na_2SO_4, and evaporated in vacuo. The resulting product (**9**) was used in the next step without further purification. TFA (3.3 μL, 0.0429 mmol, 0.2 equiv) was added to a solution of **9** in pyrrole (1.6 mL, 12.9 mmol, 60 equiv) at room temperature under N_2. After stirring for 105 min, the reaction was quenched with 0.1 M aqueous NaOH. The organic phase was washed with water, dried over Na_2SO_4, and evaporated in vacuo. The residue

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was purified by silica gel column chromatography using hexane/CH_2Cl_2 = 1/1 (v/v) as eluent. The first fraction afforded **10** (145 mg, 84.3%): ^{1}H NMR ($CDCl_3$, 300 MHz, ppm) δ 5.83 (s, 1H), 5.94 (br s, 2H), 6.04 (br s, 2H), 6.16−6.18 (m, 2H), 6.52 (br s, 2H), 6.70 (br s, 2H), 7.87 (br s, 2H), 8.06 (br s, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz, ppm) δ 31.6, 31.7, 33.0, 107.6, 107.7, 107.9, 108.6, 116.2, 118.2, 124.0, 124.1, 124.2, 124.3, 127.8, 128.4, 128.5 (the signals due to the pentafluorophenyl moieties could not be assigned because of the complicated multiple coupling of ^{13}C−^{19}F). Anal. Calcd for $C_{37}H_{17}F_{15}N_4$: C, 55.37; H, 2.14; N, 6.98. Found: C, 55.76; H, 2.30; N, 6.89; R_f = 0.50 (hexane/CH_2Cl_2 = 1/4 (v/v)).

C-Fused Norrole (12). A 50 mL CH_3CN solution of **8** (50 mg, 0.0623 mmol) and *p*-TsOH•H_2O (3.23 mg, 0.0188 mmol) were stirred at ambient temperature for 1 h. Then, the reaction mixture was added dropwise to a stirred solution of DDQ (50 mg, 0.220 mmol) in CH_3CN (50 mL) under reflux. After 2 h, the solvent was evaporated in vacuo. The residue was passed through an alumina column and further purified by silica gel column chromatography using hexane/CH_2Cl_2 = 3/2 (v/v) as eluent. The green fraction afforded **12** (1.0 mg, 2.0%): ^{1}H NMR ($CDCl_3$, 300 MHz, ppm) δ 7.10−7.14 (m, 1H), 7.22 (d, J = 4.2 Hz, 1H), 7.81 (d, J = 4.2 Hz, 1H), 7.85 (d, J = 4.2 Hz, 1H), 8.05 (d, J = 4.2 Hz, 1H), 8.16−8.20 (m, 1H), 8.39 (d, J = 4.2 Hz, 1H), 8.96 (br s, 1H), 10.0 (br s, 1H); ^{19}F NMR ($CDCl_3$, 282 MHz, ppm) δ −136.5 (dd, J = 22.6, 6.7 Hz, 2F), −138.3 (dd, J = 22.6, 7.9 Hz, 2F), −140.5 (dd, J = 23.2, 7.3 Hz, 2F), −151.0 (t, J = 20.8 Hz, 1F), −152.7 (t, J = 21.4 Hz, 1F), −154.9 (t, J = 21.4 Hz, 1F), −160.3 (td, J = 21.7, 6.5 Hz, 2F), −161.47 (td, J = 22.0, 7.5 Hz, 2F), −161.50 (td, J = 22.0, 7.5 Hz, 2F); (CH_2Cl_2, λ_{max}/nm) 404.0, 430, 606.0; HRMS (ESI$^-$) found m/z 793.04845, calcd for $C_{37}H_8F_{15}N_4$ ([M − H]$^-$) m/z 793.05094; R_f = 0.50 (hexane/CH_2Cl_2 = 1/1).

■ ASSOCIATED CONTENT

Supporting Information. Spectroscopic data of new compounds. Details on theoretical studies and X-ray analysis. This material is available free of charge via the Internet at http://pubs.acs.org.

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