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Confusion and Neo-Confusion: Corrole Isomers with an NNNC Core**

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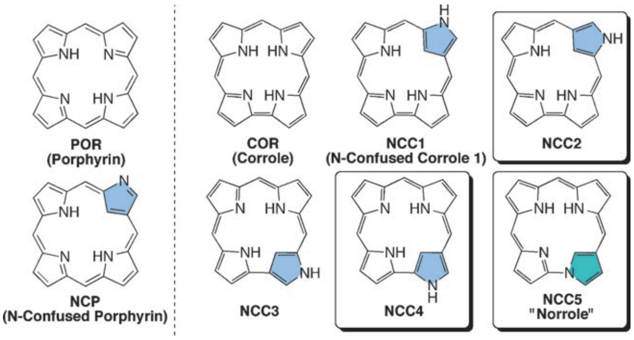
Corrole is a class of contracted porphyrin with an NNNN donor core and containing a direct pyrrole–pyrrole link in the molecular skeleton.[1] Since the first synthesis by Johnson and Kay in 1965,[2] the unique properties of corrole, and especially its metal coordination chemistry, which is different from that of regular porphyrin, has received much attention.[3] Because of the recent improvement on the triaryl corrole synthesis, corrole chemistry, and in particular the corrole-based applications, have been progressively developed.[4]

Our group has been involved in the porphyrin analogue chemistry, and especially that of confused porphyrinoids, since the discovery of the porphyrin isomer, N-confused porphyrin (NCP).[5] This porphyrin mutant possesses an NNNC core owing to the presence of α,β′-linked (so-called confused) pyrrole ring in the framework, which dramatically alters its properties, reactivity, and coordination chemistry.[6] The unexpectedly rich chemistry of NCP inspired us to explore other confused porphyrinoids, which we call the "confusion approach".[6b] Until now, various confused expanded porphyrinoids, such as sapphyrin, pentaphyrin, and hexaphyrin, have been successfully synthesized and their peculiar chemistry revealed.[6c] The chemistry of contracted tetrapyrrolic macrocycle, on the other hand, remains unexplored owing to the presence of a set of confused isomers (**NCC1**-**4**) which have an NNNC core with different arrangement of the confused pyrrole ring.[7] This time we have succeeded in synthesizing two of them (**NCC2** and **NCC4**), and an unprecedented *N*-linked isomer (**NCC5**), to which the trivial name norrole is given (Scheme 1). Herein, the details of the structures and properties are described.



Scheme 1. Synthesis of N-confused corroles.

Details of the synthesis are outlined in Scheme 2. Because the initial attempt for condensation reactions of N-confused dipyrromethane dicarbinol (**1**) with 2,2′-bipyrrole (**2**) did not work well, intramolecular oxidative cyclization reactions of N-confused bilanes were examined. Thus, the reaction of **1** with pyrrole provided 7-aza-22-carbabilane (**3**) in 89 % yield, and the reaction of N-confused dipyrromethane monocarbinol (**4**) with dipyrromethane (**5**) afforded 1-aza-21-carbabilane (**6**) in 69 % yield. Subsequent oxidation of bilane **3** with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) in CH_3CN afforded **NCC2-C_6F_5** in 5 % yield. Meanwhile, the oxidation of bilane **6** with DDQ provided **NCC4-C_6F_5** in 18 % yield, together with **NCC5-C_6F_5** in 1 % yield. The addition of a halide anion did not improve the yields, in contrast to the case of regular corrole.[8]

In the ^{1}H NMR spectrum of **NCC2-C_6F_5** (**NCC4-C_6F_5**) in $CDCl_3$, a relatively sharp singlet owing to the interior CH proton was observed at $\delta = -0.91$ (1.84) ppm, and broad resonances attributed to the interior NH protons were observed at $\delta = 2.61$ (4.12) and 5.72 (8.04) ppm, while the peripheral NH proton appears at $\delta = 9.38$ (9.24) ppm. The ^{1}H NMR data suggest that both isomers are aromatic and adopt the inner-3H form (with three hydrogen atoms inside the core, as shown in Scheme 2) in $CDCl_3$ solution; this observation is consistent with the theoretical estimation on the relative stability of NH tautomers.[9,10] The ^{13}C NMR signal that is ascribable to the inner CH of **NCC4-C_6F_5** was observed in an up-field region at $\delta = 91.24$ ppm, which is much higher than other peripheral CH signals observed at $\delta >$ 100 ppm, reflecting the ring current effect.[5a] One characteristic difference between **NCC5-C_6F_5** and the other NCCs is the number of pyrrolic CH protons in the ^{1}H NMR spectra: nine ^{13}C signals for C−H groups, rather than eight in all other cases, were observed in the DEPT 90 measurement; eight of the signals appear between $\delta = 6.27$–7.90 ppm, while the unique signal is at $\delta = 1.21$ ppm.

The explicit structures of **NCC2-C_6F_5**, **NCC4-C_6F_5**, and **NCC5-C_6F_5** were elucidated by the X-ray crystallographic analyses (Figure 1).[11] All of the carbon and nitrogen atoms

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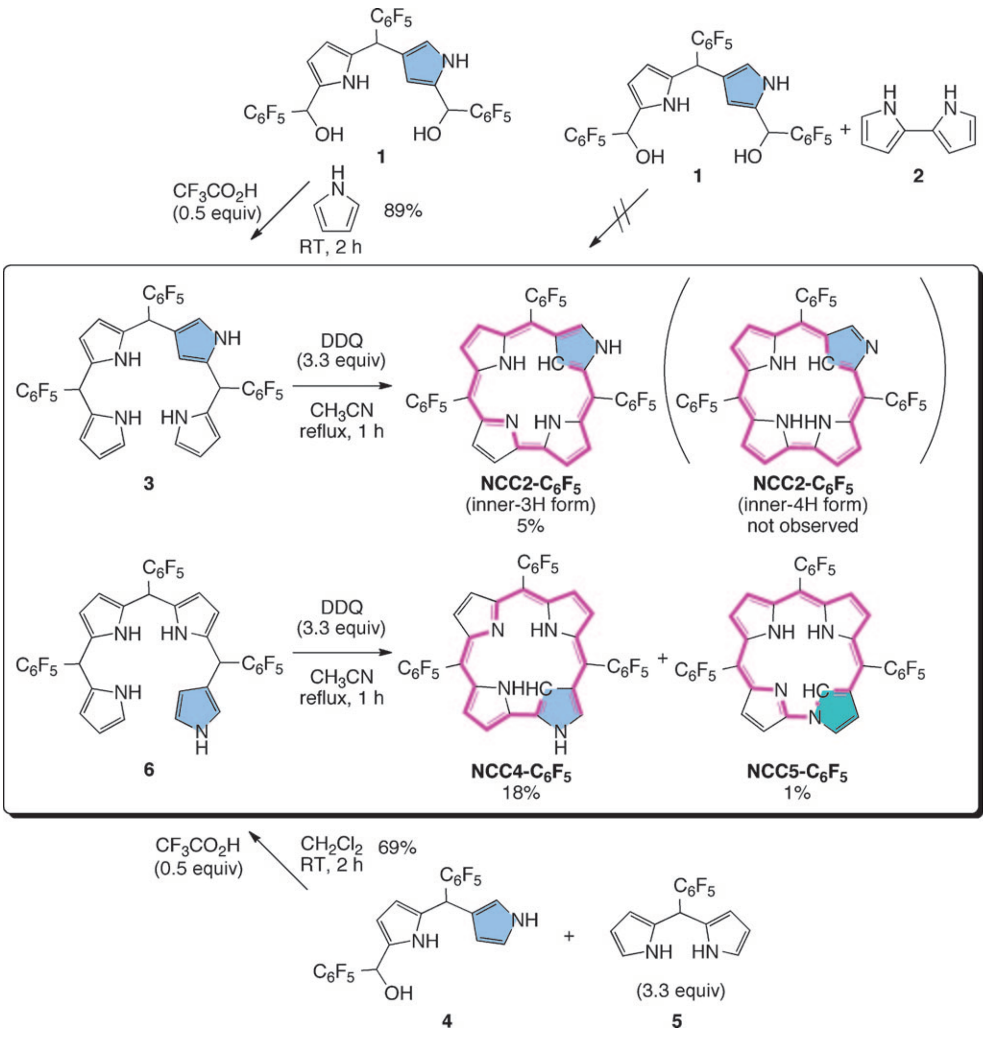

Scheme 2. Structures of porphyrin and corrole isomers.

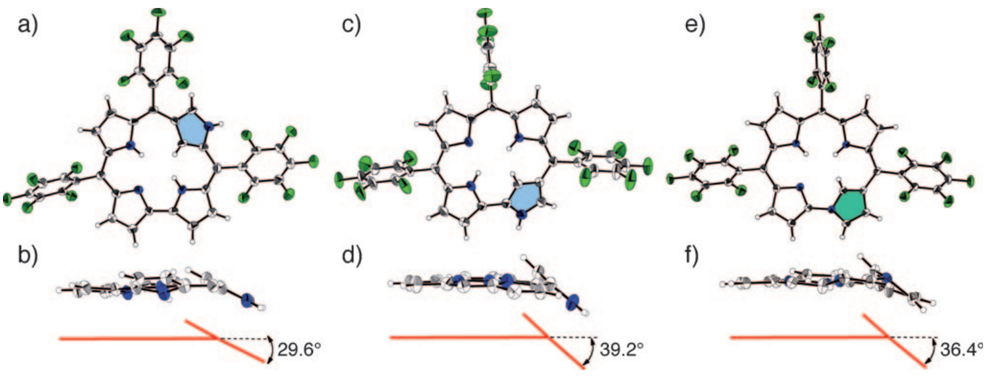

Figure 1. X-ray structures of corrole isomers: a,b) **NCC2-C$_6$F$_5$**, c,d) **NCC4-C$_6$F$_5$**, e,f) **NCC5-C$_6$F$_5$**. Thermal ellipsoids are set at 30% probability; C$_6$F$_5$ groups are omitted for clarity in views (b,d,f). N blue, C black, F green.

can be clearly distinguished from the differences in electron density, and all of the hydrogen atoms are found in the Fourier maps, which imply the inner-3H forms of **NCCs**, being consistent with the C-N-C bond angles, in the solid state. Consequently, the nitrogen atoms of outward-pointing confused pyrroles of **NCC2-C$_6$F$_5$** and **NCC4-C$_6$F$_5$** are protonated (that is, amino type). In all NCCs, the confused (α,β′-linked) and neo-confused (N,β-linked) pyrrole rings are tilted significantly from the corrole plane composed of the remaining 18 heavy atoms: namely 29.6° (**NCC2-C$_6$F$_5$**), 39.2° (**NCC4-C$_6$F$_5$**), and 36.4° (**NCC5-C$_6$F$_5$**), and the remaining tripyrrole units adopt a nearly planar conformation, a situation that is different from relatively planar **COR-C$_6$F$_5$**.[12] The larger distortion of the planarity of **NCC4-C$_6$F$_5$** could explain its weaker aromaticity than **NCC2-C$_6$F$_5$**.

The absorption and emission spectra of NCCs in CH$_2$Cl$_2$ are shown in Figure 2, and the numerical data are summarized in Table 1. Compared to the parent **COR-C$_6$F$_5$**, significant red-shifts in the absorption spectra are observed for NCCs. In particular, the red-shift of as much as 130 nm is observed for **NCC2-C$_6$F$_5$**. Nevertheless, the absorption coefficients of the Q-type bands are similar to each other. Meanwhile, the Soret-type bands of NCCs are split, unlike in **COR-C$_6$F$_5$**. In the fluorescence spectra, a distinct emission was observed in a series of NCCs with comparable or smaller absolute emission quantum yields (Φ_{em}). Among the NCCs, **NCC5-C$_6$F$_5$** shows the highest Φ_{em} of 5.7% in CH$_2$Cl$_2$, and **NCC2-C$_6$F$_5$** and **NCC4-C$_6$F$_5$** show the Φ_{em} of 1.0% and 1.4%, respectively. A remarkable feature of NCCs is indicated by their large Stokes shifts (774–1445 cm^{-1}) compared to the corresponding regular corrole (221 cm^{-1}). Because no significant difference is recognized in their molecular orbitals (see below), the large Stokes shifts would not be responsible in intramolecular charge transfer but could be due to the flexibility of macrocycles. Furthermore, upon protonation with CF$_3$CO$_2$H, large red-shifts were observed in the Q-bands

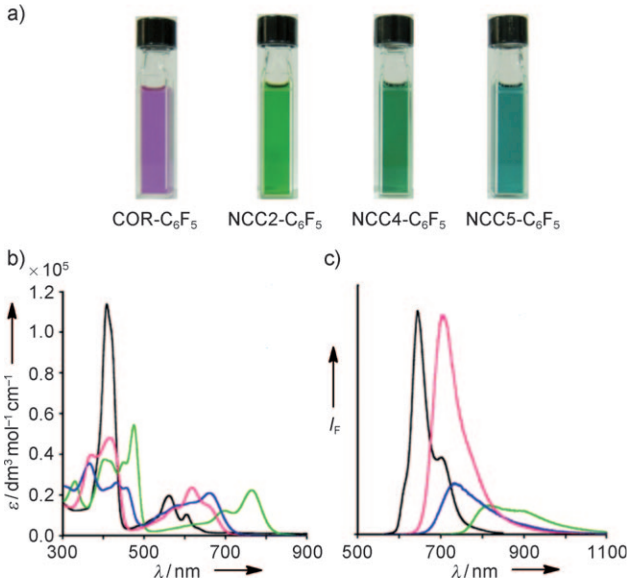

Figure 2. Solution colors and spectra of the corrole and corrole isomers in CH$_2$Cl$_2$: a) solution color, b) absorption, c) emission. (Black line COR-C$_6$F$_5$, green line NCC2-C$_6$F$_5$, blue line NCC4-C$_6$F$_5$, red line NCC5-C$_6$F$_5$).

Table 1: Optical properties of NCCs in CH$_2$Cl$_2$.

Structure	λ_{abs}[a] [nm]	Δ_{HL}[b] [eV]	λ_{em}[c] [nm]	Φ_{em}[d]	Stokes shift [cm^{-1}]	λ_{abs}[e] [nm]
COR-C$_6$F$_5$	634[f]	2.53	643	0.070	221	622
NCC2-C$_6$F$_5$	764	1.85	812	0.010	774	792
NCC4-C$_6$F$_5$	662	2.14	732	0.014	1445	782
NCC5-C$_6$F$_5$	659[f]	2.23	705	0.057	990	735

[a] The lowest energy absorption maxima. [b] Theoretical HOMO–LUMO gaps. [c] The wavelength of emission maxima. Excited at the Soret-like band. [d] Absolute quantum yields. [e] The values for NCCs monoprotonated with CF$_3$CO$_2$H. [f] Shoulder.

of NCCs: 28 nm (**NCC2-C$_6$F$_5$**), 120 nm (**NCC4-C$_6$F$_5$**), and 76 nm (**NCC5-C$_6$F$_5$**), while a small blue-shift (12 nm) was observed for **COR-C$_6$F$_5$**. Such red-shifts could be rationalized by a loss of planarity owing to the absence of intramolecular hydrogen bonding and also the steric congestion inside the NCC core.[13]

Molecular orbitals and HOMO–LUMO orbital energies calculated at the B3LYP/6-31G** level are shown in Figure 3. The theoretical HOMO–LUMO energy gaps of NCCs (1.85–2.23 eV) are considerably smaller than that of the regular corrole (2.53 eV) and in good agreement with their absorption spectra (Table 1). Narrow HOMO–LUMO energy gaps of NCCs are attributable mainly to the rise in the HOMO energy level. In the HOMO of **COR-C$_6$F$_5$**, a large contribution is observed at the four inner nitrogen atoms. Confusion of **COR-C$_6$F$_5$** represents replacement of one inner nitrogen atom by the carbon atom without significant change in the shape of HOMO. As a result, the HOMOs of NCCs would be destabilized owing to less electronegativity of the carbon atom than the nitrogen atom. In all of the HOMOs and LUMOs, no significant localization of the molecular orbital coefficients is recognized, which suggests negligible intramolecular charge transfer nature in the HOMO–LUMO transitions. In contrast, slight localization is observed in LUMO + 1. Compared to nearly degenerated HOMO and HOMO−1 of **COR-C$_6$F$_5$**, degeneracy is lost in NCCs, which would account for the split Soret-like bands of NCCs.

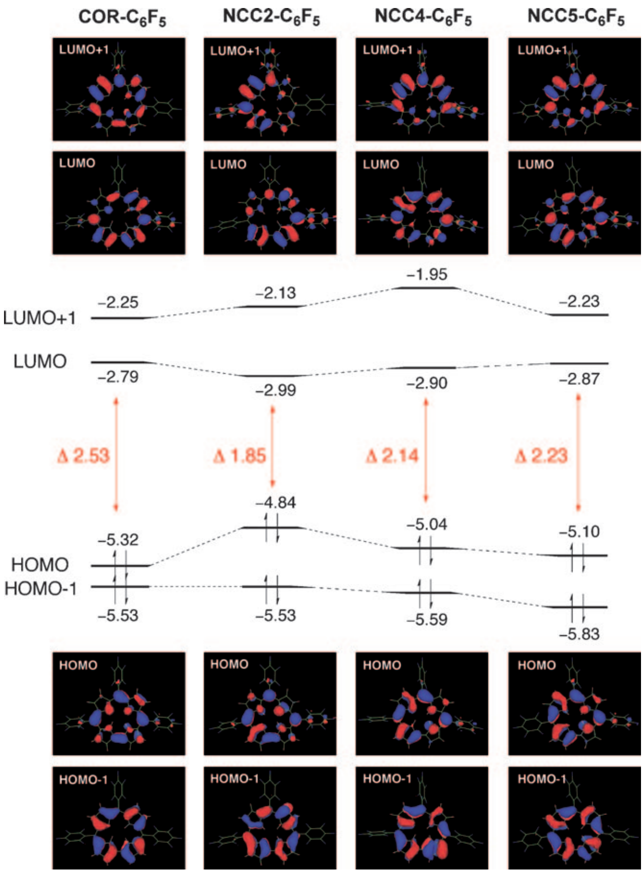

Figure 3. Kohn–Sham orbitals and orbital energy levels [eV] of corrole and NCCs.

The aromaticity of NCCs was evaluated with the aid of ^{1}H NMR chemical shifts, nucleus-independent chemical shift (NICS)[14] values, and harmonic oscillator model of aromaticity (HOMA)[15] indices (Table 2). In the ^{1}H NMR spectra, maximum difference between the chemical shifts of peripheral CH moieties and those of interior CH or NH moieties ($\Delta\delta_{\text{CH-CH}}$ or $\Delta\delta_{\text{CH-NH}}$) was utilized to evaluate the strength of the aromatic ring current. Because the chemical shifts of the NH protons are influenced by intramolecular hydrogen bonding, the $\Delta\delta_{\text{CH-CH}}$ values would be more reliable, though the $\Delta\delta_{\text{CH-NH}}$ values are described owing to the absence of

Table 2: Evaluation of aromaticity in NCCs.

Structure	$\Delta\delta_{\text{CH-CH}}$ [ppm]	$\Delta\delta_{\text{CH-NH}}$ [ppm]	NICS [ppm]	HOMA$_{\text{all}}$	HOMA$_{18}$
POR-C$_6$F$_5$	–	11.9	−13.4686	0.642	0.809
NCP-C$_6$F$_5$	14.2	11.5	−12.1474	0.654	0.807
COR-C$_6$F$_5$	–	11.3	−12.1363	0.726	0.789
NCC2-C$_6$F$_5$	9.3	5.8	−6.8208	0.631	0.707
NCC4-C$_6$F$_5$	5.7	3.5	−4.8230	0.646	0.645
NCC5-C$_6$F$_5$	6.7	6.8	−7.2753	0.669	0.711

interior CH moiety in the regular porphyrin. Both **POR-C$_6$F$_5$** ($\delta = 11.9$ ppm) and **COR-C$_6$F$_5$** ($\delta = 11.3$ ppm) shows the large $\Delta\delta_{\text{CH-NH}}$ values, indicating strong aromaticity. Similarly, **NCP-C$_6$F$_5$** also shows strong aromaticity ($\Delta\delta_{\text{CH-CH}}$: 14.2 ppm, $\Delta\delta_{\text{CH-NH}}$: 11.5 ppm). **NCC2-C$_6F_5$**, **NCC4-C$_6F_5$**, and **NCC5-C$_6F_5$** have smaller $\Delta\delta_{\text{CH-CH}}$ ($\Delta\delta_{\text{CH-NH}}$) values of 9.3 (5.8) ppm, 5.7 (3.5) ppm, and 6.7 (6.8) ppm, respectively. Thus NCCs are moderately aromatic from the viewpoint of ^{1}H NMR spectra. In accordance with the $\Delta\delta$ values, the NICS values of **NCC2-C$_6$F$_5$** (−6.8208 ppm) and **NCC5-C$_6$F$_5$** (−7.2753 ppm) indicate moderate aromaticity, and that of **NCC4-C$_6$F$_5$** (−4.8230 ppm) indicates weak aromaticity. On the other hand, the HOMA indices, the structural aspects of aromaticity, for [18]annulenic moiety (HOMA$_{18}$) seem also applicable in the present system, although the indices for all the corrole or porphyrin core (HOMA$_{\text{all}}$) are not informative. The HOMA$_{18}$ of around 0.8 (**POR-C$_6$F$_5$**, **NCP-C$_6$F$_5$**, **COR-C$_6$F$_5$**) represents strong aromaticity and of around 0.7 (**NCC2-C$_6$F$_5$**, **NCC5-C$_6$F$_5$**) moderate aromaticity. The HOMA$_{18}$ of 0.645 for **NCC4-C$_6$F$_5$** denotes weak aromaticity.

As shown above, the photophysical properties and the aromaticity of NCCs differ appreciably depending on the position of the confused pyrrole ring. Such a difference is also reflected in the anion-binding behavior (Figure 4). The neutral **NCC2-C$_6$F$_5$** and **NCC4-C$_6$F$_5$** possess the peripheral NH moieties that can bind anions through hydrogen bonding, as observed for NCP,[16] whereas **NCC5-C$_6$F$_5$** and **COR-C$_6$F$_5$** lack such an NH moiety at the periphery. Thus, in the ^{1}H NMR spectra of **NCC2-C$_6$F$_5$** (**NCC4-C$_6$F$_5$**) in CDCl$_3$, the peripheral NH signal exhibits a significant low-field shift from $\delta = 9.38$ (9.24) to 14.40 (13.39) ppm upon an addition of excess amount of Bu$_4$NCl, while no characteristic spectral change was observed with **NCC5-C$_6$F$_5$** and **COR-C$_6$F$_5$**. The binding constant for Cl$^-$ (K_{Cl}) was determined to be $K_{\text{Cl}} = 3.2 \times 10^3$ L mol^{-1} (**NCC2-C$_6$F$_5$**) and $K_{\text{Cl}} = 1.6 \times 10^3$ L mol^{-1} (**NCC4-C$_6$F$_5$**), respectively, from the absorption spectral changes during the titration with Bu$_4$NCl in CH$_2$Cl$_2$. Interestingly, the anion affinity is much larger than that of NCP ($K_{\text{Cl}} = 580$ L mol^{-1}),[16b] which is ascribable to the preferred inner-3H form of NCCs that provides a peripheral NH. Moreover, the K_{Cl} value of **NCC2-C$_6$F$_5$** is larger than that of **NCC4-C$_6$F$_5$**, which is inconsistent with the estimated ion–dipole interaction,[17] and strongly infers the effective anion–π interaction in the former.[16,18] The distance between Cl$^-$ and the nearest C$_6$F$_5$ group is significantly shorter in the case of **NCC2-C$_6$F$_5$** (3.611 Å) than that of **NCC4-C$_6$F$_5$** (7.821 Å), which partially supports this proposal. Furthermore, interaction between Cl$^-$ and the neighboring C$_6$F$_5$ group in **NCC2-C$_6$F$_5$** was realized by the ^{19}F NMR spectra of **NCC2-C$_6$F$_5$**, in which the large shifts of the signals assignable to one of the C$_6$F$_5$ groups were observed by the addition of Bu$_4$NCl, whereas no significant change was detected with **NCC4-C$_6$F$_5$**.[10]

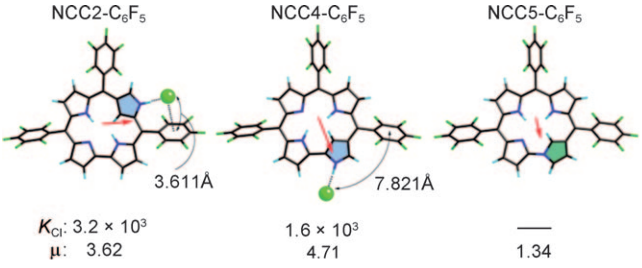

Figure 4. Anion binding behavior of NCCs. Values of the binding constant K_{Cl} are given in L mol^{-1}. The arrows indicate the direction of the dipole moment μ (values in Debye) of anion-free NCCs. See the Supporting Information for details.

In summary, we have synthesized three types of NCC isomers, and their structures and properties are revealed. The position of the confused pyrrole ring in NCC affects the optical and anion-binding properties distinctly. Owing to the presence of a carbon atom inside the core of NCCs, rich coordination chemistry could be expected for NCCs like the case of NCP.[19] Furthermore, the finding of an *N*-linked isomer, norrole, could open a way to a new porphyrinoid chemistry. Further studies, including the metal coordination chemistry, is now underway.

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[11] Crystal data for **NCC2**: green prisms, C$_{37}$H$_{11}$F$_{15}$N$_4$, $M_r = 796.50$, triclinic, space group $P\bar{1}$, $a = 8.551(3)$, $b = 14.231(5)$, $c = 14.501(5)$ Å, $\alpha = 116.864(6)$, $\beta = 100.597(7)$, $\gamma = 95.456(7)°$, $V = 1515.0(9)$ Å^3, $Z = 2$, $T = 223$ K, $R = 0.0774$, w$R = 0.1872$ (all data), GOF = 1.010. **NCC4**: dark green blocks,

$C_{37}H_{11}F_{15}N_4 \cdot C_7H_{16}$, $M_r = 896.70$, monoclinic, space group $P2_1/n$, $a = 15.413(2)$, $b = 10.4586(14)$, $c = 24.102(4)$ Å, $\beta = 92.159(2)°$, $V = 3882.5(9)$ Å^3, $Z = 4$, $T = 296(2)$ K, $R = 0.0670$, $wR = 0.1621$ (all data), GOF = 1.015. **NCC5**: violet prisms, $C_{37}H_{11}F_{15}N_4 \cdot 2(CH_2Cl_2)$, $M_r = 966.35$, monoclinic, space group $P2_1/c$, $a = 13.6542(8)$, $b = 13.4057(7)$, $c = 21.1649(11)$ Å, $\beta = 104.684(1)°$, $V = 3747.6(4)$ Å^3, $Z = 4$, $T = 223(2)$ K, $R = 0.0735$, $wR = 0.2229$ (all data), GOF = 1.025. CCDC 719319 (**NCC2**), 719320 (**NCC4**), and 719321 (**NCC-5**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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