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Halide Anion Mediated Dimerization of a *meso*-Unsubstituted N-Confused Porphyrin

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Abstract: The new N-confused porphyrin (NCP) derivatives, *meso*-unsubstituted β-alkyl-3-oxo N-confused porphyrin (3-oxo-NCP) and related macrocycles, were synthesized from appropriate pyrrolic precursors by a [3+1]-type condensation reaction. 3-Oxo-NCP forms a self-assembled dimer in dichloromethane that is stabilized by complementary hydrogen-bonding interactions arising from the peripheral amide-like moieties. The protonated form of 3-oxo-NCP was observed to bind halide anions (F^-, Cl^-) through the outer NH and the inner pyrrolic NH groups, thus affording a dimer in dichloromethane. The structure of the chloride-bridged dimer in the solid state was determined by X-ray diffraction analysis.

Keywords: anion binding · anion recognition · dimerization · N-confused porphyrins · porphyrins

Introduction

Anion binding by synthetic receptors has been investigated extensively in recent years. This research was motivated by the importance of anions in biological systems and the potential application of anion receptors as sensors, transporters, catalysts, and so on.[1,2] Among the various synthetic receptors for anions studied in recent years, oligopyrrolic macrocycles such as calix[4]pyrroles and expanded porphyrins, which contain the pyrrolic NH hydrogen-bond-donor groups within their cavities or cores, have received considerable attention.[3,4] As well as the internal binding normally displayed by such systems, an usual example of peripheral anion binding, which involves an outwardly pointing NH pyrrolic moiety, was reported recently in the case of the modified porphyrinoids, N-confused porphyrins (NCPs; Scheme 1).[5] In spite of the fact that NCPs provide but a single hydrogen-bond-donor site, they were found to bind halide anions tightly, presumably due to the well-oriented molecular dipole moment directed toward the peripheral

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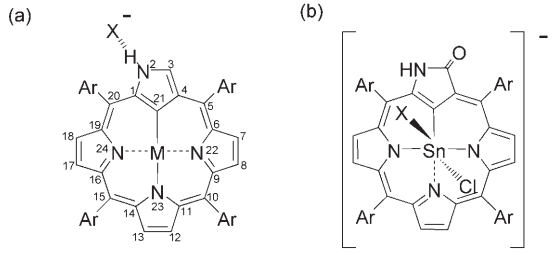


Scheme 1. Anion-binding modes stabilized by N-confused tetraarylporphyrins; these involve interactions at a) the periphery and b) a coordinated metal center. M = H_2, Ni^{II}, Pd^{II}, Cu^{II}; X = halide anion (F^-, Cl^- in the present study).

NH group and the large polarizability of the molecule.[6] Interestingly, internal anion binding by NCPs was observed in the case of the Sn^{IV} complex of 3-oxo-substituted N-confused tetraarylporphyrins. In this case, which has considerable precedence in metalloporphyrin chemistry,[7] the anion was found to be coordinated as an axial ligand to the Sn^{IV} center.[8] Due to the special nature of NCPs (they have NH hydrogen-bond donors on both the interior and exterior of the macrocyclic ring), the metal-free form of NCPs was also expected to interact with anions through the inner NH groups.[9] Depending on the extent to which this occurs, a new type of anion binding might be established, whereby an anion guest is recognized by different NH-derived binding modes, internal or external, or some combination thereof. Intrigued by such a possibility, we sought a system in which such flexible recognition could be explored and, accordingly, report herein the first study of the anion-binding properties of a β-alkyl-3-oxo N-confused porphyrin (3-oxo-NCP). This system, studied in the form of its HF, HCl, and $HBPh_4$ salts, was found to form an anion-mediated dimer both in dichloromethane solution and in the solid state.

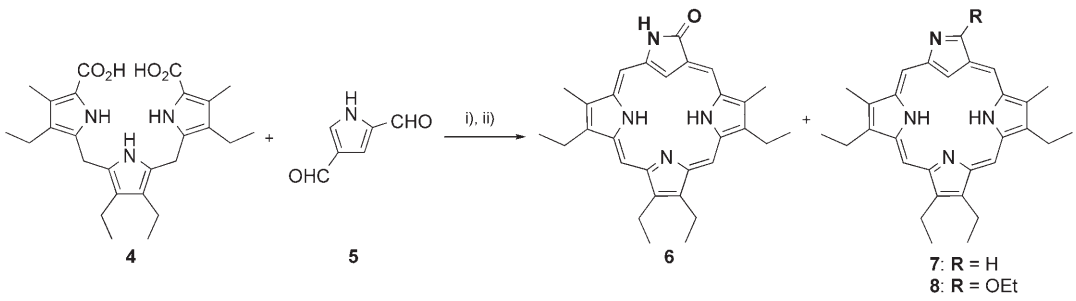
Results and Discussion

Synthesis of β-Alkyl-3-oxo N-confused Porphyrin

Meso-unsubstituted β-hepta- and hexaalkylated N-confused porphyrins were synthesized by Dolphin and co-workers by using a MacDonald-type [2+2] approach,[10] and by Lash et al. with a [3+1] condensation reaction.[11] We also adopted a [3+1] reaction leading to products **6**–**8** (Scheme 2). Briefly, a solution in ethanol of tripyrrane diacid (**4**)[12] and 2,4-diformylpyrrole (**5**),[13] the same precursors used by the Lash group, was stirred for 12 h in the presence of *p*-toluenesulfonic acid. After oxidation with *o*-chloranil, the reaction mixture was purified by column chromatography over silica gel (eluent: 2% MeOH in CH_2Cl_2). The first red band contained a small amount of 2,8,12,17-tetraethyl-3,7,13,18-tetramethylporphyrin (<1%), whereas the ensuing three red-brown bands were found to correspond to the 3-oxo (**6**, 6%),[14] 3-ethoxy (**8**, 1%), and expected 3-H (**7**, 3%)[11a] species. When rigorously dried anhydrous ethanol was used as the solvent during the condensation, the yield of **6** decreased to 0.5%, whereas the amount of ethoxy-substituted product **8** increased to 9%. Thus, while the mechanism of the substitution of the confused pyrrole ring remains to be clarified, we consider it likely that the 3-oxo substituent arises from adventitious moisture present in the solvent.[7,15]

The *meso*-free N-confused porphyrins **6**–**8** displayed ^{1}H NMR signals characteristic of such species, namely, resonances ascribable to the *meso* protons and the inner C21H protons at $\delta = 9$–10 ppm and $\delta = -6.87$, -6.41, and -6.74 ppm, respectively, in $CDCl_3$. Furthermore, 3-oxo-NCP (**6**) displayed a broad ^{1}H NMR signal at $\delta = 9.22$ ppm as well as a ^{13}C NMR signal at $\delta = 171.1$ ppm; these features are ascribable to an amide-like moiety (NH–CO). More direct support for the structure of **6** came from a single-crystal X-ray diffraction analysis of the monohydrochloride salt (**6**·HCl) (see below). Specifically, the observed carbon–oxygen bond length (C3–O) was 1.216(6) Å, a value typical for a C=O bond.[16]

The amide-like form of **6** was dominant in a range of solvents, including C_6D_6, CD_3OD, C_5D_5N, and $[D_6]$DMSO (DMSO = dimethyl sulfoxide), on the basis of the ^{1}H NMR spectra. The chemical shift of the N2H proton was dependent on the temperature and concentration. As the concentration increased or the temperature decreased, the N2H signal shifted to lower field, for example, from $\delta = 8.98$ ppm (0.34 mM) to $\delta = 9.04$ ppm (1.0 mM), whereas the chemical shifts of other peripheral proton signals were relatively small (Figure 1). The temperature- and concentration-dependent chemical shifts of the N2H signal were considered consistent with a self-dimerization process, in which a dimer of **6** is formed through complementary hydrogen-bonding interactions involving the amide-like moieties (Scheme 3). From the chemical shifts of the N2H proton signal at various concentrations, the dimerization constant (K_d) associated with this presumed dimerization was estimated to be $26\,M^{-1}$ (at 30°C in CD_2Cl_2); this value compares favorably to those recorded for an N-confused calix[4]phyrin with an identical 3-oxo moiety at the confused pyrrole ring ($14\,M^{-1}$) and a species for which such a dimerization process was previously established.[17,18]



Scheme 2. Synthesis of β-alkyl-3-oxo-NCP (**6**). The [3+1] condensation reaction of precursors **4** and **5** shown also produces the N-confused porphyrins **7** and **8**, although in lower yields (6, 3, and 1% for **6**, **7**, and **8**, respectively). Reaction conditions: i) *p*-toluenesulfonic acid/EtOH, 12 h, room temperature; ii) *o*-chloranil, 4 h, room temperature.

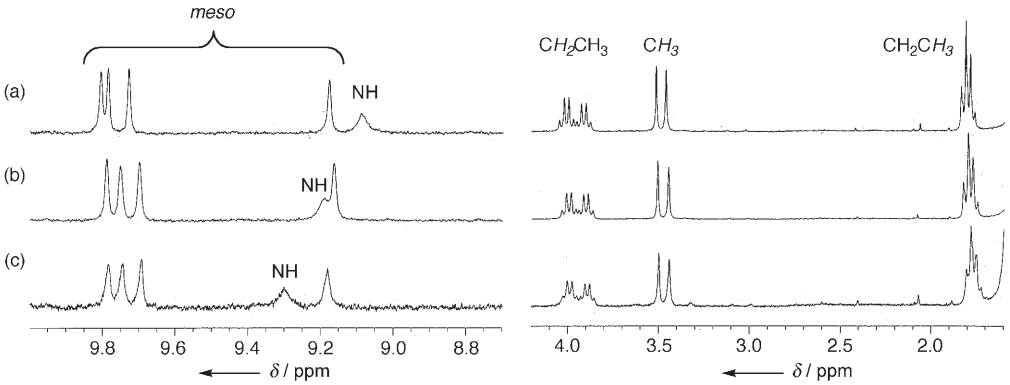
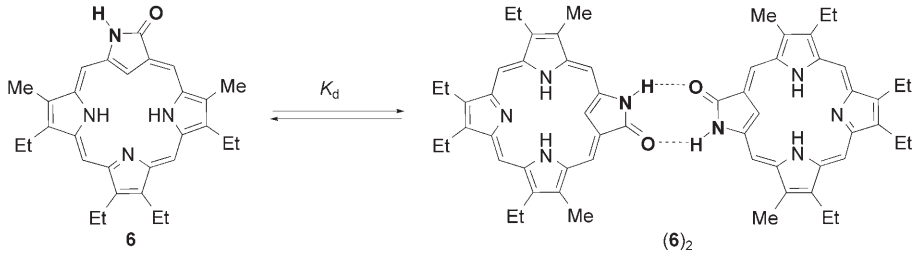


Figure 1. ^{1}H NMR spectra of 3-oxo-NCP (**6**) in $CDCl_3$ at a) 30 °C, b) 10 °C, and c) −10 °C.



Scheme 3. Self-dimerization of 3-oxo-NCP (**6**) resulting from complementary hydrogen bonding.

Dimer Formation Mediated by Halide Anions in the Solid State

Ditopic interactions in the core and the periphery of NCPs can be used for constructing self-assembled supramolecules. For example, self-assembled dimers and trimers were fabricated by simultaneous metal coordination at the inner and outer nitrogen atoms of NCPs.[19] In the present system, the peripheral amide-like and inner NH atoms could act as recognition sites for typical pyrrole NH hydrogen-bond acceptors such as the halide anions chloride and fluoride.

Previously, the diprotonated sapphyrin was shown to bind halide anions through interactions with the five NH donor groups present within the core.[4] Owing to the contribution of electrostatic terms, the anion-binding affinities observed for this and other protonated oligopyrrolic macrocycles are usually much larger than those for the corresponding (or analogous) neutral species. Thus, for the present anion-binding study, we prepared three protonated salts of **6** (**6**·HCl, **6**·HF, and **6**·$HBPh_4$); these were generated by washing the metal-free form with an excess of HCl, HF, and $HBPh_4$, respectively.

In the case of **6**·HCl, recrystallization from dichloromethane/diethyl ether gave rise to single crystals suitable for X-ray diffraction analysis (Table 1). The resulting structure revealed that **6**·HCl crystallizes in the form of a chloride anion bridged dimer (Figure 2). Here, each chloride anion (two per dimer, one per monoprotonated macrocycle) is bound, through hydrogen-bonding interactions, to the three central pyrrole rings of one macrocycle and the amide-like NH group of the second (the relevant pyrrole NH···Cl distances are 2.43, 2.24, and 2.31 Å, whereas the peripheral N2H···Cl distance is 2.30 Å). The net result is a dimer in which the chloride anion, located 2.42 Å above the N_3C core of one of the macrocycles and displaced 6.99 Å from the center of the other N_3C core, serves to glue the two NCP subunits together. Although such dimerization motifs have been observed in the case of self-assembling "tailed" sapphyrins and calix[4]pyrroles,[20] to the best of our knowledge they are unknown in the context of simple porphyrinoids.

Table 1. Summary of crystallographic data for **6**·HCl.

Compound	**6**·HCl
Formula	$C_{33}H_{35}N_4OCl$
M_r	503.07
Crystal size [mm^3]	0.17×0.17×0.51
Crystal system	monoclinic
Space group	$P2_1/n$ (No. 14)
a [Å]	10.929(2)
b [Å]	15.160(2)
c [Å]	16.429(2)
α [°]	90
β [°]	101.87(1)
γ [°]	90
V [Å^3]	2663.8(7)
ρ_{calcd} [g cm^{-3}]	1.26
Z	4
T [K]	183
No. of reflections	10472
No. of unique reflections	6060
$\lambda(Mo_{K\alpha})$ [Å]	0.71073
R_1 ($I>4\sigma(I)$)	0.0816
wR_2 ($I>4\sigma(I)$)	0.188
GOF	1.015

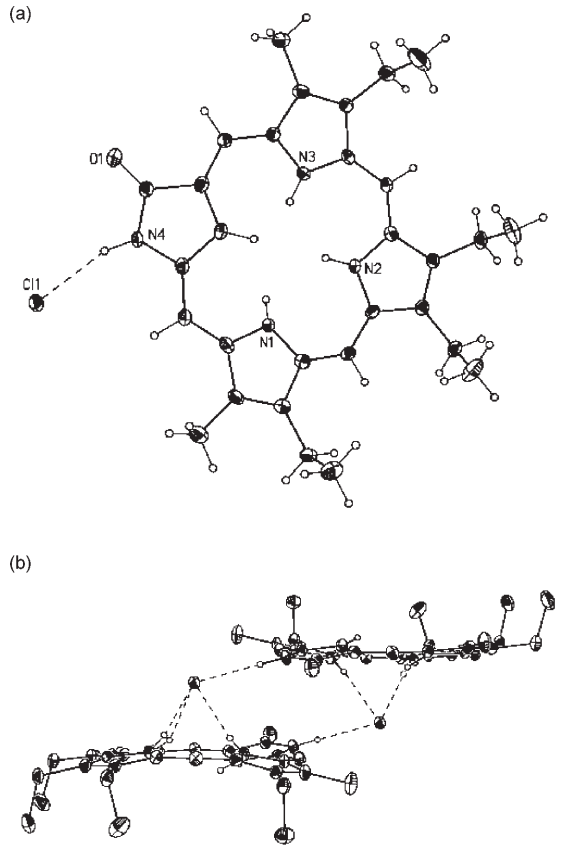


Figure 2. a) View of $(C_{22}H_{35}N_4O)^+Cl^-$ (**6**·HCl) showing a partial atom-labeling scheme. Thermal ellipsoids are drawn at the 30% probability level. Hydrogen atoms shown are drawn to an arbitrary scale. The chloride ion is within H-bonding distance of N4 with the following relevant geometry: N4–H4···Cl1: N···Cl 3.197(4) Å, H···Cl 2.30(4) Å, N–H···Cl 162(3)°. b) Dashed lines illustrate the H-bonding interactions: N1–H1···Cl1: N···Cl 3.276(4) Å, H···Cl 2.43(6) Å, N–H···Cl 165(5)°; N2–H2···Cl1: N···Cl 3.130(4) Å, H···Cl 2.24(4) Å, N–H···Cl 166(4)°; N3–H3···Cl1: N···Cl 3.142(4) Å, H···Cl 2.31(6) Å, N–H···Cl 150(5)°.

Dimer Formation Mediated by Halide Anions in Solution

To examine whether **6**·HCl might exist as a dimer in solution, vapor pressure osmometry (VPO) experiments were carried out in dichloromethane ([**6**·HCl] = 0.4–3.2 mM). These analyses revealed an average solution-phase molecular weight of 836 ± 20 for **6**·HCl (calcd for monomer **6**·HCl: 503.1; calcd for dimer $(\mathbf{6}\cdot HCl)_2$: 1006.2). These findings are thus consistent with this salt being partially, but not completely, dimerized in this particular halocarbon solvent.

Further support for the proposed dimeric nature of **6**·HCl and **6**·HF came from electron-spray ionization mass spectrometric (ESI-MS) analyses (see Supporting Information, Figure S4). In particular, ESI-MS of a solution of **6**·HCl in dichloromethane gave rise to peaks at $m/z = 969.5$ ($[(\mathbf{6}\cdot HCl)_2 - HCl]^+$, 7%), 933.6 ($[(\mathbf{6}\cdot HCl)_2 - 2HCl]^+$, 40%), and 467.1 ($[\mathbf{6}+H]^+$, 100%). Similar results were obtained for **6**·HF; in this case, peaks at $m/z = 952.6$ ($[(\mathbf{6}\cdot HF)_2 - HF]^+$, 100%), 933.6 ($[(\mathbf{6}\cdot HF)_2 - 2HF]^+$, 89%), and 467.1 ($[\mathbf{6}+H]^+$, 91%) were observed. In the case of **6**·$HBPh_4$, on the other hand, an intense ion peak at $m/z = 467.3$ ($[\mathbf{6}+H]^+$, 100%) along with a small anion-free dimer peak at $m/z = 933.6$ ($[(\mathbf{6}\cdot HBPh_4)_2 - 2HBPh_4]^+$, 7.5%) were observed. These findings thus support the proposal that the HF salt is also dimerized in dichloromethane solution and/or in the gas phase.

Further structural analysis in solution was made by ^1H NMR spectroscopy (Figure 3). The analysis of **6**·HCl, carried out at 20°C in CD_2Cl_2, revealed the presence of four internal (1 × CH and 3 × NH) protons resonating at $\delta = -6.60$, -1.92, -1.24, and -0.55 ppm and an outer NH signal at $\delta = 8.85$ ppm. When analogous studies were made by using the mono-$HBPh_4$ salt of **6**, the corresponding peaks were found at $\delta = -6.58$, -3.58, -3.27, -2.76, and 11.34 ppm, respectively. By contrast, the mono-HF salt (**6**·HF) displayed signals for the inner hydrogen atoms, split by ^{19}F–^1H coupling, that resonated at considerably higher field ($\delta = -9.90$, -7.81, -7.43, and -6.93 ppm).

The signals of **6**·HCl and **6**·HF shifted upfield can be rationalized in terms of the ring-current effect of the neighbor-

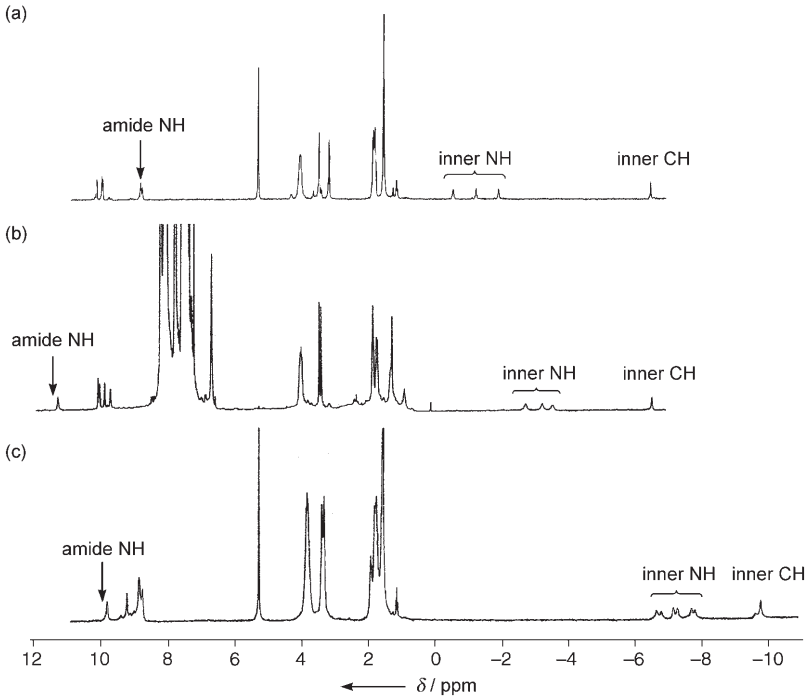
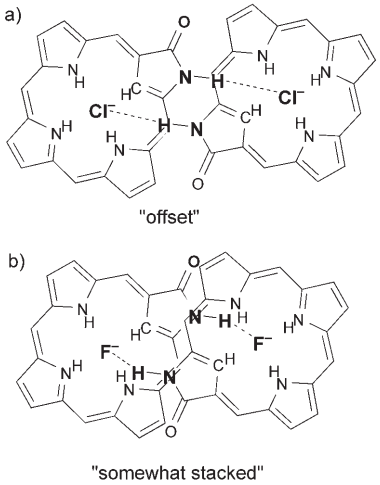


Figure 3. ^1H NMR spectra of a) **6**·HCl, b) **6**·$HBPh_4$, and c) **6**·HF.

ing porphyrin. By assuming a model whereby the $HBPh_4$ salt is not appreciably dimerized, the ^1H NMR spectroscopic data are consistent with the HCl salt being dimerized in an "offset" manner, whereas the HF salt is dimerized in a "somewhat-stacked" fashion (Scheme 4). The "offset"



Scheme 4. Plausible halide-mediated dimerization modes of a) **6**·HCl and b) **6**·HF in dichloromethane.

dimerization mode proposed for **6**·HCl is analogous to that seen in the solid state and would explain the deshielding effects observed in the ^1H NMR spectrum. By contrast, the "somewhat-stacked" geometry proposed for the HF salt is reasonable given the smaller ionic radius of F^- and its increased propensity to form hydrogen bonds; it is also consistent with the shielding effects observed in the ^1H NMR spectrum of **6**·HF.[21]

More structural information was obtained by analyzing the chemical shifts of particular peripheral protons as a function of temperature. While most of the peripheral and inner proton signals of **6**·HCl were found to give rise to shifts that were independent of temperature, large changes were observed for the amide-like NH (H^1), *meso*-H (H^2), and methyl-H (Me^1) resonances (Figure 4a–c). In particular, the H^2 and Me^1 signals, which were well-resolved, shifted to higher field as the temperature decreased. Such a result is rationalized in terms of the enhanced diamagnetic ring-current effect that results from the stabilization of the "offset" dimer at the lower-temperature region. On the other hand, in the case of the $HBPh_4$ salt of **6**, such a large chemical-shift change of Me^1 was not observed (Figure 4e). These results thus further support the proposed anion-mediated dimerization of **6**·HCl (but not that of **6**·$HBPh_4$) in dichloromethane.

Besides the above first-order dimerization process, a detailed analysis of the change in the chemical shift of the H^1 signal of **6**·HCl provides support for the existence of another type of dimerization process that could be operative in solution (Figure 4a). Specifically, the shift versus temperature profile of H^1 displays a maximum at around −10 °C. Upfield shifts similar to those seen for the H^1 signal of **6**·HCl in the

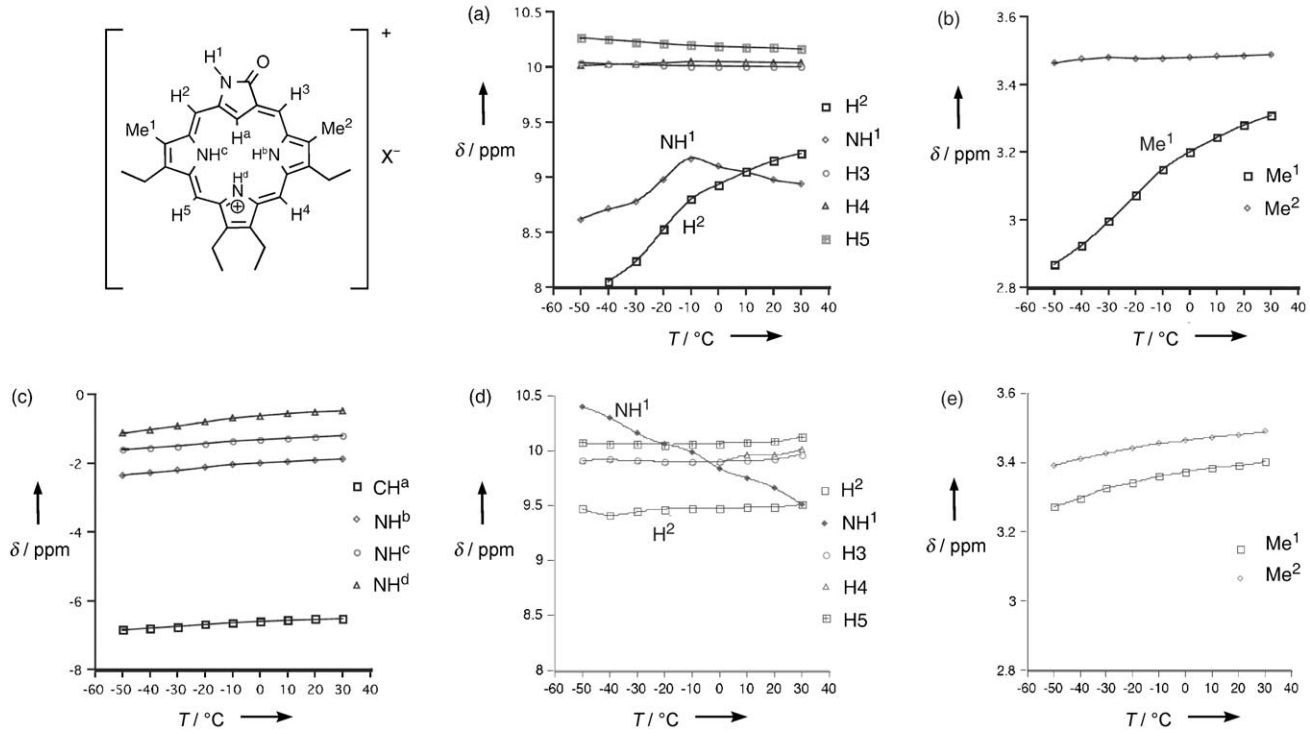


Figure 4. Changes in the chemical-shift values of the ^1H NMR signals of **6**·HCl and **6**·$HBPh_4$ recorded in CD_2Cl_2 as a function of temperature. a) Amide-like NH and *meso*-H ($X^- = Cl^-$). b) Me H ($X^- = Cl^-$). c) Inner H ($X^- = Cl^-$). d) Amide-like NH and *meso*-H ($X^- = BPh_4^-$). e) Me H ($X^- = BPh_4^-$).

lower-temperature regime were also observed for H^2 and Me^1, although the effect is far less obvious (slight deviation in the curve rather than an observable maximum). These combined chemical-shift effects can be explained by the enhanced formation of the anion-mediated dimer in the low-temperature region as the dominant process, as well the formation of an amide-linked dimer analogous to that seen for the free-base form of **6** (see above). This combination of factors would give rise to effects that are different for the two sets of signals (H^1 vs. H^2 and Me^1), with one set (H^1) being more sensitive to amide-mediated dimer formation and the other (H^2 and Me^1) a more accurate indicator of anion-binding-triggered dimerization. It also helps to rationalize the negative slope of the chemical-shift changes observed in the higher-temperature region as this can be ascribed to the formation of a dimer mediated by hydrogen-bonding interactions involving the amide-like moieties, rather than NH–anion binding. This is apparently seen with the H^1 signal of **6**·$HBPh_4$ (Figure 4c). In other words, on the basis of these findings, we propose that two types of dimers, one that is anion-mediated and the other based on amide–amide hydrogen-bonding interactions, compete with one another and with the monomeric **6**·HCl salt in dichloromethane, and that the anion-mediated dimer, which is more stable than the hydrogen-bonded amide–amide dimer, is dominant at lower temperatures (Scheme 5). Unfortunately, a similar analysis for the **6**·HF salt was hampered by its low solubility, which caused severe broadening of the ^{1}H NMR signals at lower temperatures.

Conclusions

A *meso*-unsubstituted 3-oxo N-confused porphyrin (3-oxo-NCP), **6**, was synthesized as the major isolable product of a [3+1] condensation reaction involving pyrrolic precursors. The free-base form of 3-oxo-NCP (**6**) afforded a dimer in dichloromethane that is stabilized by complementary hydrogen-bonding interactions resulting from the peripheral amide-like moieties. In contrast, the protonated form of 3-oxo-NCP (HCl and HF salts) gave rise to a different type of dimer bridged by the counter halide anions. An X-ray structure of the chloride anion mediated dimer (**6**·HCl)$_2$ reveals clearly that the halide anion is bound by both the inner and peripheral NH groups of the protonated macrocycle. By extending the results found herein, specifically by using one or more outer amide-like groups as hydrogen-bond-donor "sticky sites", it may be possible to construct porphyrin-like arrays containing modified NCP cores. On a different level, porphyrinoids such as **6**, specifically modified at key peripheral positions, could prove useful as receptors for more complex anions, including biologically important ones such as nucleotides and N-protected amino acids.[22] We are currently exploring these possibilities.

Experimental Section

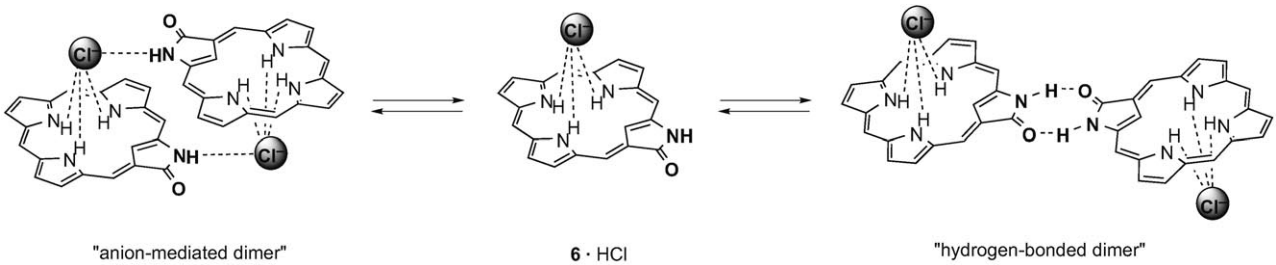
General Procedures

Commercially available solvents and reagents were used without further purification unless otherwise mentioned. Silica-gel column chromatography was performed on Wakogel C-200 and C-300. Thin-layer chromatography (TLC) was carried out on aluminum sheets coated with silica gel 60 (Merck 5554). UV/Vis spectra were recorded on PerkinElmer Lambda 19 and Shimadzu UV-3150PC spectrometers. ^{1}H and ^{13}C NMR spectra were recorded on JEOL JNM-AL300, Bruker RX300 (operating at 270.17 MHz for ^{1}H and 67.97 MHz for ^{13}C), and JEOL JMN-GSX 270 (operating at 300.00 MHz for ^{1}H and 75.47 MHz for ^{13}C) spectrometers with deuterated chloroform as the internal lock and residual solvent as the internal reference. Fast atom bombardment mass spectrometry (FAB-MS) was carried out on a JEOL-HX110 mass spectrometer in the positive-ion mode with a 3-nitrobenzylalcohol matrix. ESI mass spectra were obtained on a Perkin–Elmer Sciex API 300 mass spectrometer. VPO experiments were carried out on a GONOTEC OSMOMAT 070 instrument. Elemental analysis was performed at the Analytical Center at Kyushu University.

Syntheses

6, **7**, and **8**: 2,5-Bis[(5-carboxy-3-ethyl-4-methylpyrrole-2-yl)methyl]-3,4-diethylpyrrole (**4**; 1.0 mmol) and *p*-toluenesulfonic acid (4 mmol) were added to a solution of pyrrole-2,4-dicarboxaldehyde (**5**; 1.0 mmol) in ethanol (1 L). After the mixture was stirred for 12 h at room temperature in the dark under an Ar blanket, *o*-chloranil (2.0 mmol) was added. The resulting mixture was then stirred for an additional 4 h. The solvent was evaporated off by using a rotorary evaporator, and the resulting crude black mixture was purified by column chromatography over silica gel (eluent: 2% MeOH/CH_2Cl_2). Fractions were isolated as described in the text.

6: 2H,7,18-Dimethyl-8,12,13,17-tetraethyl-3-oxo-2-aza-21-carbaporphyrin: Red-green solid. M.p. > 300 °C; UV/Vis (CD_2Cl_2): λ_{max} (log ε) = 415.5 (5.30), 425 (sh), 513 (4.2), 549.5 (4.2), 603 (3.8), 664 nm (3.9); ^{1}H NMR (270 MHz, $CDCl_3$): $\delta = -6.87$ (s, 1H, C21H), −4.00 (br s, 2H, NH), 1.74–1.85 (m, 12H, CH_2CH_3), 3.43 (s, 3H, CH_3), 3.51 (s, 3H, CH_3), 3.95–4.10 (m, 8H, CH_2CH_3), 9.12 (s, 1H, *meso*-H), 9.59 (br s, 1H, NH), 9.64 (s, 1H, *meso*-H), 9.68 (s, 1H, *meso*-H), 9.86 ppm (s, 1H, *meso*-H); ^{1}H NMR (300 MHz, [D_6]DMSO, 303 K): $\delta = -7.06$ (s, 1H, C21H), −4.30 (br s, 2H,



Scheme 5. Solution-phase dimerization processes involving the hydrochloride salt of 3-oxo-NCP (**6**·HCl).

NH), 1.79–1.84 (m, 12H, CH_2CH_3), 3.52 (s, 3H, CH_3), 3.55 (s, 3H, CH_3), 3.91–3.93 (m, 4H, CH_2CH_3), 4.04–4.08 (m, 4H, CH_2CH_3), 9.26 (s, 1H, *meso*-H), 9.59 (s, 1H, *meso*-H), 9.63 (s, 1H, *meso*-H), 9.68 (s, 1H, *meso*-H), 11.98 ppm (s, 1H, NH); ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 11.1, 11.2, 17.2, 17.3, 18.4, 18.4, 19.5 (2C), 19.9 (2C), 91.6, 95.7, 97.2, 98.4, 102.6 (C21), 125.8, 131.0, 133.4, 134.2, 134.7 (2C), 136.0, 136.8, 138.1, 138.6, 144.2, 144.6, 152.1, 153.3, 171.1 ppm; ^{13}C NMR (75.47 MHz, [D_6]DMSO, 303 K): δ = 10.9 (2C), 17.3, 17.4, 18.6, 18.6, 18.7, 18.8, 19.1 (2C), 92.0, 95.1, 96.9 (2C), 102.5 (C21), 126.1, 130.9, 132.6, 133.3, 134.7, 134.9, 136.2, 137.0, 137.9, 138.3, 143.3, 143.9, 150.7, 151.2, 170.6 ppm; MS (FAB): *m*/*z* = 467 $[M+1]^+$; elemental analysis: calcd (%) for $C_{30}H_{34}N_4O$: C 77.22, H 7.34, N 12.01; found: C 76.74, H 7.32, N 11.15.

6·HCl: 2H,7,18-Dimethyl-8,12,13,17-tetraethyl-3-oxo-2-aza-21-carbaporphyrin hydrochloride salt: UV/Vis (CH_2Cl_2): λ_{max} = 423.3, 450.4, 548.1, 617.1, 662.0 nm; ^{1}H NMR (300 MHz, CD_2Cl_2): δ = −6.54 (s, 1H), −1.92 (s, 1H), −1.24 (s, 1H), −0.55 (s, 1H), 1.80–1.88 (m, 12H), 3.22 (s, 3H), 3.52 (s, 3H), 4.08–4.10 (m, 8H), 8.85 (br s, 1H), 8.90 (s, 1H), 10.03 (s, 1H), 10.06 (s, 1H), 10.22 ppm (s, 1H).

6·HF: 2H,7,18-Dimethyl-8,12,13,17-tetraethyl-3-oxo-2-aza-21-carbaporphyrin hydrofluoride salt: UV/Vis (CH_2Cl_2): λ_{max} = 423.6, 449.9, 545.0, 618.2, 662.5, 725.0 nm; ^{1}H NMR (300 MHz, CD_2Cl_2): δ = −9.90 (d, *J* = 31 Hz, 1H), −7.81 (d, *J* = 32 Hz, 1H), −7.43 (d, *J* = 41 Hz, 1H), −6.93 (d, *J* = 44 Hz, 1H), 1.57–1.94 (m, 12H), 3.35 (s, 3H), 3.42 (s, 3H), 3.87 (br s, 8H), 8.82–8.93 (m, 4H), 9.59 ppm (d, *J* = 180 Hz, 1H).

6·$HBPh_4$: 2H,7,18-Dimethyl-8,12,13,17-tetraethyl-3-oxo-2-aza-21-carbaporphyrin hydrotetraphenylborate salt: UV/Vis (CH_2Cl_2): λ_{max} = 423.0, 450.0, 549.5, 616.5, 662.0 nm; ^{1}H NMR (300 MHz, CD_2Cl_2): δ = −6.58 (s, 1H), −3.62 (br s, 1H), −3.30 (br s, 1H), −2.78 (br s, 1H), 1.73–1.86 (m, 12H), 3.42 (s, 3H), 3.48 (s, 3H), 4.02–4.10 (m, 8H), 8.51–6.62 (m, 20H), 9.77 (s, 1H), 9.94 (s, 1H), 10.09 (s, 1H), 10.11 (s, 1H), 11.34 ppm (s, 1H).

7: 7,18-Dimethyl-8,12,13,17-tetraethyl-2-aza-21-carbaporphyrin: Purple solid. M.p. > 300 °C; UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 418.5 (5.28), 514 (4.3), 551.5 (4.1), 615.5 (3.6), 679.5 nm (3.7); ^{1}H NMR (270 MHz, $CDCl_3$): δ = −6.41 (s, 1H, C21H), −3.90 (br s, 2H, NH), 1.77–1.84 (m, 15H, CH_2CH_3), 3.49 (s, 3H, CH_3), 3.56 (s, 3H, CH_3), 3.82–4.03 (m, 8H, CH_2CH_3), 9.53 (s, 2H, *meso*-H), 9.61 (s, 1H, *meso*-H), 9.78 (s, 1H, *meso*-H), 10.09 ppm (s, 1H, *meso*-H); ^{13}C NMR (75.48 MHz, $CDCl_3$): δ = 11.1, 11.1, 17.1, 17.2, 18.3, 18.3, 19.3, 19.4, 19.8 (2C), 94.3, 95.5, 101.0 (C21), 103.9, 107.7, 132.7, 134.8, 135.0, 135.0, 135.8, 137.6, 138.0, 138.3, 145.1, 145.6, 149.3, 154.6, 155.5, 156.4 ppm; elemental analysis: calcd (%) for $C_{30}H_{34}N_4$: C 79.96, H 7.61, N 12.43; found: C79.65, H 7.63, N 12.06.

8: 7,18-Dimethyl-3-ethoxy-8,12,13,17-tetraethyl-2-aza-21-carbaporphyrin: Red-green solid. M.p. > 238–243 °C (decomp.); UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 361 (4.4), 420 (4.9), 444.5 (4.4), 512 (4.0), 554 (3.9), 603 (3.7), 662 nm (3.5); ^{1}H NMR (270 MHz, $CDCl_3$): δ = −6.74 (s, 1H, C21H), −4.40 (br s, 1H, NH), 1.78–1.81 (m, 12H, CH_2CH_3), 1.91 (t, *J* = 7.3 Hz, 3H, OCH_2CH_3), 3.44 (s, 3H, CH_3), 3.50 (s, 6H, CH_3), 3.79–3.97 (m, 8H, CH_2CH_3), 5.20 (q, *J* = 7.2 Hz, 2H, OCH_2CH_3), 9.38 (s, 1H, *meso*-H), 9.56 (s, 1H, *meso*-H), 9.61 (s, 1H, *meso*-H), 9.83 ppm (s, 1H, *meso*-H); ^{13}C NMR (75.48 MHz, $CDCl_3$): δ = 11.1, 11.1, 15.2, 17.1, 17.3, 18.3, 18.4, 19.2, 19.4, 19.7, 29.7, 65.4, 93.9, 96.3, 98.4, 103.8 (C21), 104.3, 124.9, 132.4, 133.2, 134.5, 134.9, 135.8, 136.7, 137.2, 137.9, 143.8, 144.7, 146.2, 152.3, 153.9, 171.1 ppm; MS (FAB): *m*/*z* = 495 $[M+1]^+$; elemental analysis: calcd (%) for $C_{32}H_{38}N_4O$: C 77.70, H 7.74, N 11.33; found: C 77.24, H 7.75, N 11.07.

Single-Crystal X-ray Diffraction Analysis

Crystals grew as very dark needles by vapor diffusion of diethyl ether into a solution of $(C_{33}H_{35}N_4O)^+Cl^-$ in CH_2Cl_2/CH_3OH. A needle of approximate dimensions 0.17 × 0.17 × 0.51 mm^3 was chosen for data acquisition. Data were collected at −90 °C on a Siemens P4 diffractometer equipped with a Nicolet LT-2 low-temperature device and with a graphite monochromator with $Mo_{K\alpha}$ radiation (λ = 0.71073 Å). Details of crystal data, data collection, and structure refinement are listed in Table 1. Four reflections (3,1,0; 2,1,3; 3,0,3) were remeasured every 97 reflections to monitor instrument and crystal stability. A smoothed curve of the intensities of these checked reflections was used to scale the data. The scaling factor ranged from 0.9758 to 1.008. The data were corrected for Lp effects but not for absorption. Data reduction, decay correction, and structure solution and refinement were performed with the SHELXTL/PC software package.[23] The structure was solved by direct methods and refined by full-matrix least-squares on F^2 with anisotropic displacement parameters for the non-H atoms. The hydrogen atoms on carbon (except for C17) were calculated in idealized positions (C–H 0.96 Å) with isotropic displacement parameters set to 1.2 × U_{eq} of the attached atom (1.5 × U_{eq} for methyl hydrogen atoms). The hydrogen atoms on C17 and the nitrogen atoms were obtained from a ΔF map and refined with isotropic displacement parameters. The function $\Sigma w(|F_0|^2-|F_c|^2)^2$, in which $w = 1/[(\sigma(F_0))^2+(0.0553P)^2+(0.9462P)]$ and $P = (|F_0|^2+2|F_c|^2)/3$, was minimized. The data were corrected for secondary extinction effects. The correction took the form $F_{corr} = kF_c/[1+5.2(6)\times10^{-6}\times F_c^2\lambda^3/\sin2\theta]^{0.25}$, in which *k* is the overall scale factor. Neutral-atom-scattering factors and values used to calculate the linear absorption coefficient were obtained from the International Tables for X-ray Crystallography (1992).[24] Other computer programs used are listed elsewhere.[25] CCDC-640769 (**6**·HCl) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre at http://www.ccdc.cam.ac.uk/data_request/cif.

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