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1,3-Dipolar Cycloaddition of 2,6-Dichlorobenzonitrile Oxide to 2-Methyl-N-confused Porphyrin. Regio- and Stereoselective Synthesis and Structural Characterization of 2-Aza-21-carbabacteriochlorin and Resolution of 2-Aza-21-carbachlorin Enantiomers

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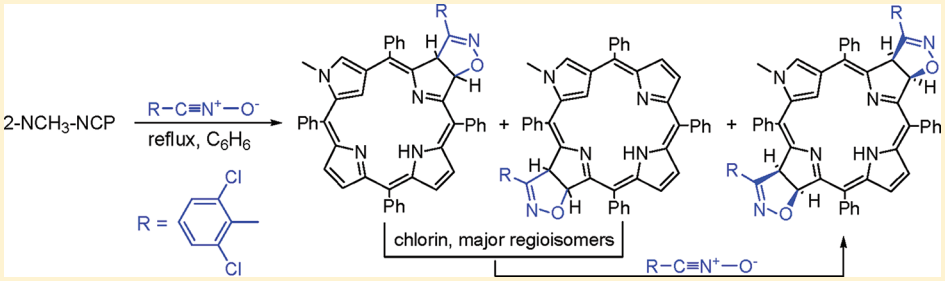
Supporting Information



ABSTRACT: The 1,3-dipolar cycloaddition reaction of 2-methyl-N-confused porphyrin with 2,6-dichlorobenzonitrile oxide yielded four isomeric monoadducts of carbachlorin type and one diadduct of carbabacteriochlorin type. Two major carbachlorin products, constituting 82% of the monoadducts, were shown to be structural precursors of the unique 2-aza-21-carbabacteriochlorin. Enantiomers of the most abundant isomer of 2-aza-21-carbachlorin (55% of all carbachlorin products) have been resolved. The crystal structures of 2-aza-21-carbabacteriochlorin and the most abundant isomer of 2-aza-21-carbachlorin were characterized by X-ray diffraction.

INTRODUCTION

For some time, tetrapyrrolic macrocycles have attracted attention owing to their versatile coordination, acid−base, optical, or redox properties which can be exploited in a broad spectrum of molecular and supramolecular systems. Porphyrins and their isomers and analogues constitute a class of stable yet relatively easily adaptable macrocycles which allows fine-tuning of their properties to a desired purpose. The robust character of the porphyrin ring which is stable toward many aggressive factors such as strong acids, bases, or oxidants is a consequence of its aromaticity. However, the delocalization pathway defining aromatic character of the porphyrins involves only 18 out of 22 π-electrons present on the macrocycle's perimeter (Figure 1). Thus, reactivity of some fragments of the porphyrin ring may resemble that of the olefins including addition reaction taking place on the two "ethylene bridges" excluded from the delocalization pathway.

Consequently, the pyrrole β,β'-positions are prone to various types of pericyclic reactions including Diels−Alder[1−3] or dipolar cycloadditions.[4,5] The resulting chlorins, bacteriochlorins, or isobacteriochlorins bearing fused exocyclic rings preserve their macrocyclic aromaticity although the ring current effect in them is reduced with respect to that observed for the porphyrin

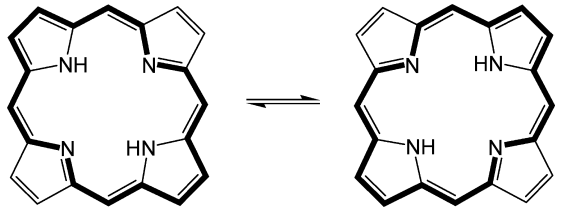


Figure 1. Delocalization path of π-electrons in the porphyrin ring.

(Figure 2). Their optical properties, characterized by a near-infrared absorption, are beneficial for photodynamic therapy application.[6]

N-Confused porphyrin (NCP) **1** is a tetrapyrrolic isomer of the regular porphyrin in which the basic skeleton of the macrocyclic ring is retained (Scheme 1).[7−9] However, placement of one of the nitrogens on the perimeter and one of the carbons inside the macrocycle considerably changes the reactivity of the ring with respect to that of the porphyrins. The numerous modifications of the NCP ring that have been

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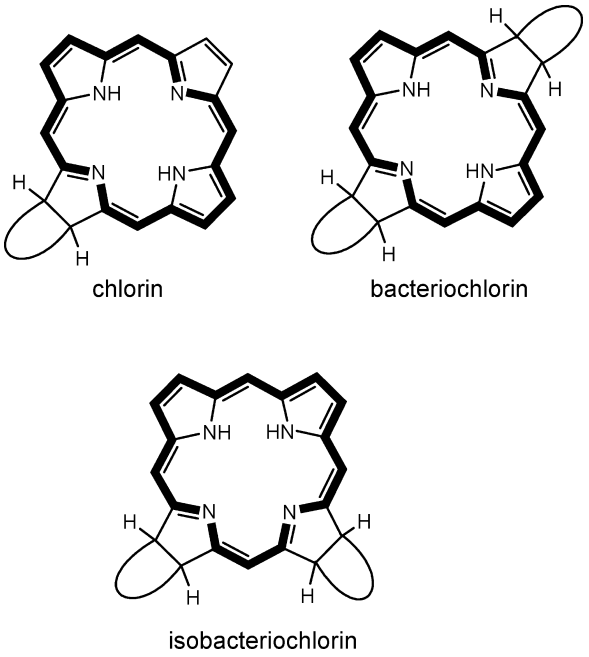
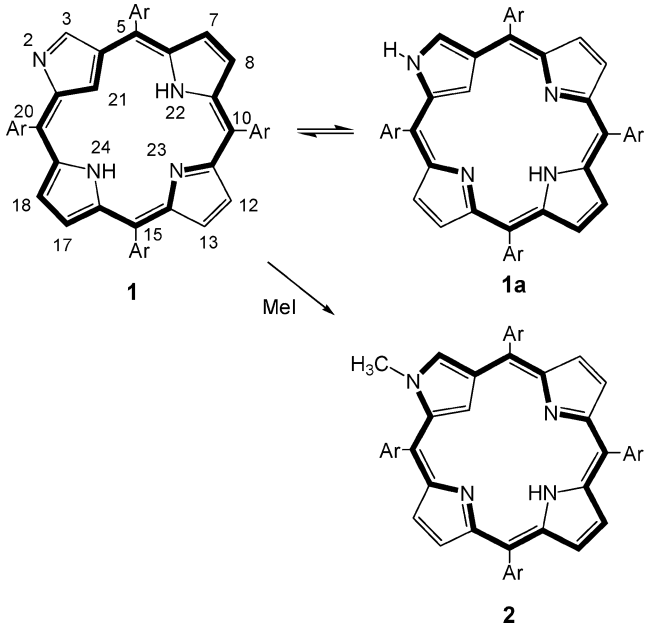


Figure 2. Schematic structures of chlorin, bacteriochlorin, and isobacteriochlorin.

Scheme 1. π-Electron Delocalization Pathway on the NCP's Perimeter



reported to date involve the *confused* pyrrole as a target leading to derivatives being products of substitution, addition, or oxidation reactions in position 2 (external nitrogen),[10−13] 3 (external carbon),[14−21] or 21 (internal carbon).[12,20−33] In addition, the reactions leading to the external or internal ring fusion[16,19−21,34−36] and exo- or endocyclic extension of the macrocycle ring system[11,37−39] took place with the participation of one or two atoms of the *confused* pyrrole.

In the present paper, we concentrate on the reactivity of the "regular part" of NCP that allows synthesis of N-confused analogues of chlorins or bacteriochlorins bearing one or two exocyclic isoxazoline ring(s).[40] The first carbachlorin, i.e., chlorin analogue with carbon replacing nitrogen inside the macrocyclic crevice, had been synthesized by Lash and Hayes by a modified 3 + 1 method of the macrocyclic ring construction,[41] but there was no report to date concerning synthesis and characteristic of carbabacteriochlorin. An interesting feature of the nonplanar derivatives of NCP such as chlorins is their intrinsic chirality. Separation of enantiomers of formed carbachlorins and their optical activity is also an objective of our study as a part of a search for new chiral ligand systems.

RESULTS AND DISCUSSION

Analogously to the regular porphyrin where a fast tautomeric equilibrium is observed in solution (Figure 1), there are tautomers of NCP **1** that differ in the positions of the NH protons in the macrocycle (Scheme 1). However, while in the regular porphyrin this process leads to the effective 4-fold symmetry of the structure (D_{4h}) and equal electron density distribution among the potential reaction targets located on the pyrrole fragments, in the case of NCP the tautomers **1** and **1a** have the π-electron delocalization path involving structurally different parts of the macrocyclic ring. As has been established, tautomer **1a** with one "mobile" proton located on the external nitrogen dominates in the polar solvents such as DMF,[42] while in the less polar solvents such as haloalkanes or hydrocarbons both protons are placed inside the macrocycle. Apparently, distribution of the π-electron density in **1a** partially excludes from the aromatic pathway the β-carbons of both pyrrole fragments that are in the *cis*-position with respect to the *confused* pyrrole. Thus, the expected targets of the addition reaction should be localized on the atoms 7, 8, 17, and 18 in **1a**, while in the case of **1** addition was expected on the *confused* pyrrole (atoms 2 and 3) or on the pyrrole trans to it (carbons 12 and 13). In order to reduce the number of possible isomers we decide to conduct our study on the readily obtainable 2-N-methylated derivative of NCP **2**[10] for which distribution of the electron density resembles that of **1a**, but there is no dynamic process that would change the situation of the potential targets of the addition reaction.

We also chose a relatively stable 1,3-dipolar reagent, i.e., 2,6-dichlorobenzonitrile oxide (DCBNO), as the cycloaddition reaction with porphyrins requires conditions which are not compatible with the in situ generated substrates, widely applied in the case of dipolarophiles comprising fully isolated double bond.[43−45]

The reaction of **2** with a 6-fold excess of DCBNO (Scheme 2) yielded, after 5 h of reflux in benzene, two types of products whose compositions were identified on the basis of mass spectrometry either as mono- (grass green solution, 29%, m/z = 817.8) or diadducts (light blue solution, 20% m/z = 1005.8). The products comprising one and two isoxazoline fragments are relatively easily separable from each other and from the starting material by column chromatography. Analysis of the ^{1}H NMR spectra of the products reveals the presence of single compound **4** in the case of the fraction containing diadducts and a mixture of four NMR-distinguishable isomers **3a−d** of the molar ratio 55:27:13:5 (based on the NMR signal integrations) in the case of that containing monoadducts.

Characterization of **4** was performed in solution by means of high-resolution mass spectrometry (ESI-TOF) and NMR spectroscopy including 1D and 2D homo- and, ^{1}H,^{13}C-heteronuclear techniques allowing full assignment of resonances (see Figure S5 in the Supporting Information).

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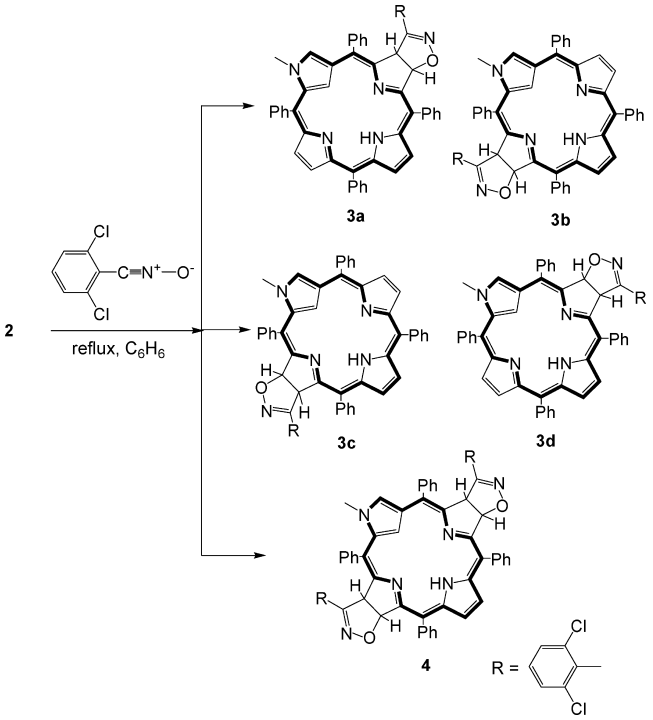
Scheme 2. Cycloaddition of DCBNO to 2-Methyl-N-confused Porphyrin



It should be noted that there are several possible arrangements of the system comprising NCP and two isoxazoline rings. Thus, if no regio- and stereospecificity of the reaction occurred one could expect formation of as many as eight NMR-distinct isomers (**4a**–**h**, Figure 3) whose structures differ in orientation of the additional rings with respect to each other or with respect to the macrocyclic ring. Formation of the isobacteriochlorin-type products involving positions 12 and 13 can be excluded along with the most unlikely adducts with trans-arrangement of the pyrrole β-protons at the isoxazoline rings (the concerted mechanism of the 1,3-cycloaddition prevents formation of such products). Hence, observation of only one species of the bacteriochlorin-type indicates regio- and stereospecific character of the diadduct formation in contrast to the analogous reaction of regular porphyrin which resulted in a mixture of isomers.[5]

The ^{1}H NMR spectral characteristics of **4** indicate a weak aromatic character of the macrocyclic ring which is reduced even with respect to that of the starting porphyrin **2**.[10,11] The "internal" protons 21 and 23-NH resonate at δ_H = 2.72 and 5.82 ppm, respectively ($CDCl_3$, 298 K), which means that in 2-aza-21-carbabacteriochlorin **4** these signals are about 2 and 1.5 ppm downfield shifted with respect to those observed for the porphyrin **2**. The sp^3 hybridization of carbons 7, 8, 17, and 18 can be inferred from their ^{13}C NMR chemical shifts. The signals of C7 and C18 can be found at about δ_C = 56 ppm, C8 and C17 near δ_C = 89 ppm, while "aromatic" C12 and C13 resonate at δ_C = 129.4 and 128.7 ppm, respectively. The chemical shifts of C8 and C17 as well as protons bound to these carbons are significantly higher when compared to those of C7 and C18 indicating downfield shifting influence of the oxygen atoms. Protons 7 and 18 correlate in the HMBC experiment with most low-field resonating carbons at δ_C = 166.7 and 168.4 ppm, respectively, which can be assigned to the quaternary carbons of the isoxazoline rings.

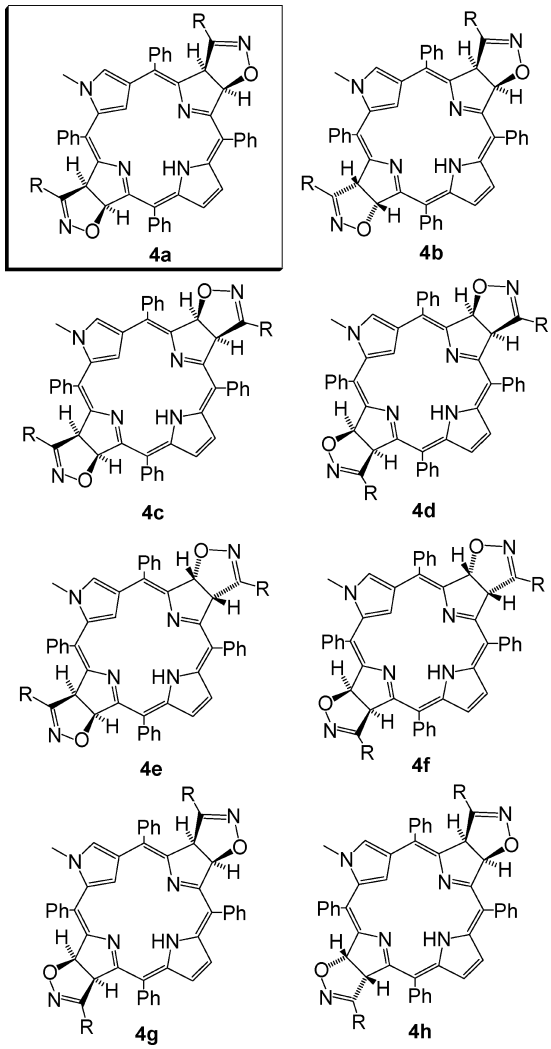


Figure 3. Eight possible isomers of carbabacteriochlorin.

Detailed analysis of the low-temperature COSY and NOESY experiments provided information concerning position and configuration of the additional rings. The hypothetical isomers **4c**–**h** whose structures comprise C7–O and/or C18–O bond(s) can be excluded from the consideration. The patterns of the through-space interactions among the protons 2-Me, 20-Ph, 18 and/or 3, 5-Ph, 7 predicted for these isomers on the basis of the PM3 energy-optimized molecular models, do not match that observed in the low-temperature NOESY. On the basis of an array of the through-space interactions between protons, we estimated interprotonic distances in **4** and compared them with those predicted for stereoisomers **4a** and **4b**. The best fit was obtained for isomer **4a**. The molecule possesses isoxazoline rings with oxygen atoms bound to C8 and C17 pyrrole β-carbons and these rings are oriented *syn* to each other.

Analysis of the single-crystal X-ray diffraction of **4** confirmed identity of the compound in the solid state (Figure 4). The *syn*-arrangement of the isoxazoline rings and formation of C8–O1 and C17–O2 bonds are apparent. The distances between the ring carbon atoms connected by single bonds are about 1.52 Å, while those being part of the aromatic system are separated by 1.34–1.41 Å (Table 1). The porphyrin ring is essentially planar except for the *confused* pyrrole fragment. The mean displacement from the plane P_{21} defined by 21 heavy atoms of the "regular" part of the ring (all NCP atoms except N2, C3 and

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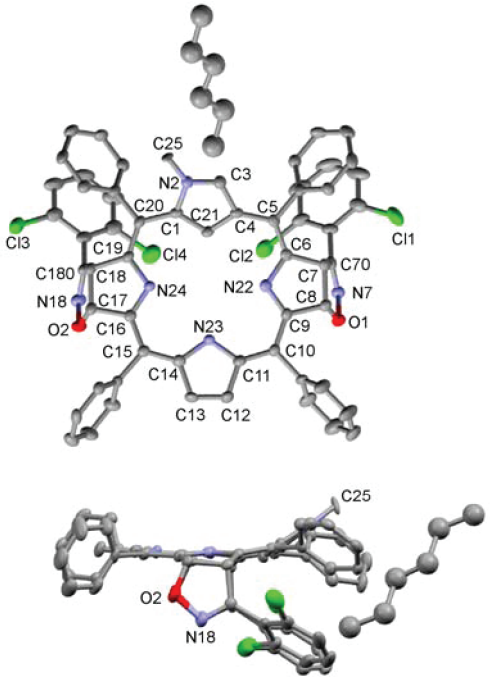


Figure 4. Perspective views of the molecular structure of **4**. All hydrogen atoms and two $CHCl_3$ solvent molecules are omitted. Thermal ellipsoids are set at the 50% probability level, except for the hexane solvent molecule. Only the dominating structure out of two which are present in the crystal lattice due to N2−C3 disorder is shown.

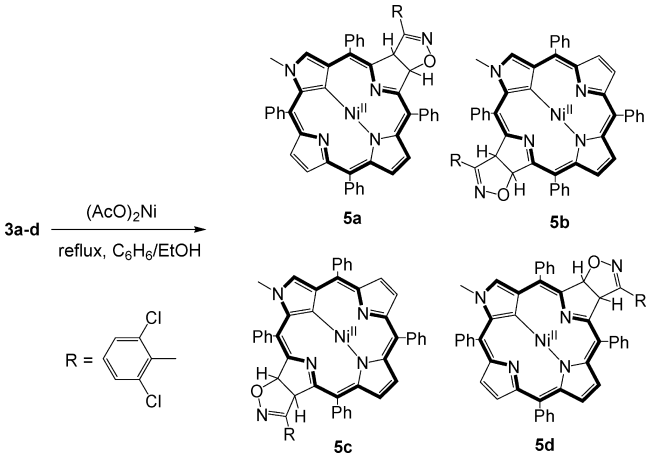
Table 1. Selected Bond Lengths from the Crystal Structures of Monoadduct 3a and Diadduct 4

	distance (Å)	
bond	**3a**	**4**
C1−N2	1.403(5)	1.419(5)
C1−C21	1.419(6)	1.397(6)
N2−C3	1.334(5)	1.342(5)
C3−C4	1.394(5)	1.400(5)
C4−C21	1.385(6)	1.414(5)
C6−C7	1.526(6)	1.524(5)
C7−C8	1.520(5),	1.521(6)
C8−C9	1.509(6)	1.520(5)
C11−C12	1.432(6)	1.441(6)
C12−C13	1.338(6)	1.344(6)
C13−C14	1.427(5)	1.429(6)
C16−C17	1.451(6)	1.519(5)
C17−C18	1.340(6)	1.519(5)
C18−C19	1.431(6)	1.531(6)
C6−N22	1.400(5)	1.387(5)
C9−N22	1.344(5)	1.317(5)
C11−N23	1.364(5)	1.387(5)
C14−N23	1.378(5)	1.386(5)
C16−N24	1.344(5)	1.330(5)
C19−N24	1.382(5)	1.396(5)

C21) is 0.162 Å, while N2 and C3 lie about 1 Å above this plane and C21 0.1 Å under P_{21}. The dihedral angle between mean plane of the *confused* pyrrole and P_{21} is 33.5°. In addition, both isoxazoline rings are planar with a mean atom displacement of about 0.05 Å. The dihedral angles between P_{21} and the mean planes of each of them are 101.0° and 103.5°. The molecule is disordered in the crystal lattice which is related to the N2−C3 permutation and displacement of the methyl group C25 over two almost equally occupied sites. Although the molecule possesses four nonequivalent stereogenic centers on the asymmetric carbons C7, C8 (*R/S*, *R/S*) and C17, C18 (*S/R*, *S/R*) it crystallizes in the centrosymmetric space group, and thus, the crystal is racemic. There is a cocrystallizing hexane solvent molecule in the crystal lattice of **4** (Figure 4). The closest distance between some of the carbons of 5- and 20-phenyl, dichlorophenyl, and confused pyrrole and those of hexane are about 3.8−3.9 Å. The crystal unit cell contains also six chloroform molecules distributed among two types of inequivalent sites. The interactions between the molecules in the crystal are all that of the van der Waals type.

In the case of the mixture of isomeric monoadducts, we encountered a serious problem in separation of the components since column chromatography, TLC, HPLC, and fractional crystallization failed. Separation and identification of these species as well as recognition of their quantitative distribution seem to be necessary in exploration of the source of selectivity observed upon the bisadduct formation. Thus, in order to establish primary target(s) of the cycloaddition we decided to transform the isomers into nickel(II) complexes and separate them in such a form by combination of a flash chromatography and HPLC on a chiral stationary phase. The metalation reaction proceeded efficiently (93% yield) in the boiling benzene/ethanol solution in the presence of about 10-fold excess of nickel(II) acetate as a metal source (Scheme 3).

Scheme 3. Metalation of Carbachlorins 3a−d



The ^{1}H NMR spectrum of the mixture of complexes **5** taken after an initial silica-gel column chromatography with dichloromethane as a mobile phase indicates the presence of four products of similar spectral patterns which differ in chemical shift and integral intensities. The mixture composition calculated on the basis of signal integrations was 57:27:9:7. A part of the major component (about 30%) can be separated from the other monoadduct complexes by flash chromatography on a densely packed SiO_2 column with toluene as an eluent. Its structure was established as **5a** by an analysis of the NMR data including low-temperature COSY and NOESY experiments. The through-space interaction between protons of 2-Me, 20-Ph, 18 on the one side of the molecule and protons 3, 5-Ph, 7 on the other allowed full assignment of the signals and thus unequivocally localized the isoxazoline ring in this product (see the Supporting Information for details).

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Free base of carbachlorin **3a** can be efficiently obtained by removing metal from the separated complex **5a** by means of concentrated hydrochloric acid followed by neutralization, extraction, and crystallization. Comparison of the ^{1}H NMR spectrum of this product with that of the mixture of isomeric chlorins indicates that this demetalation product is indeed a major chlorin-type macrocycle obtained by the 1,3-cycloaddition. The low-temperature COSY and NOESY experiments allowed assignment of the protons. The spectral pattern and through-space interactions of protons were consistent with the proposed structure of **3a**. Its aromatic character is reflected by a ring current effect which is stronger than that in **4**. The "inner" protons 21 and 23-NH resonate at δ = 1.75 and 4.50 ppm ($CDCl_3$, 300 K), respectively; i.e., they are shifted about 1 ppm upfield with respect to those observed for **4** while signals of protons localized on the ring perimeter are shifted downfield (e.g., for proton 3 $\Delta\delta$ = 0.63 ppm).

The X-ray structure of **3a** confirmed its identity in the solid state (Figure 5). There is one isoxazoline ring fused with pyrrole

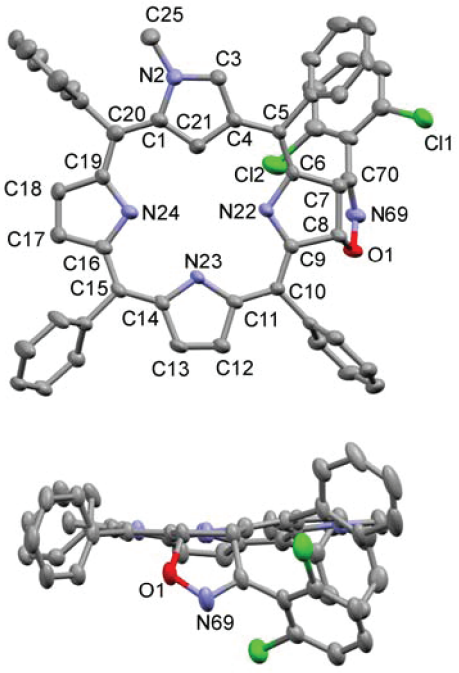

Figure 5. Perspective views of the molecular structure of **3a**. Arbitrarily, only enantiomer *SS* is shown. All hydrogen atoms are omitted for clarity. Thermal ellipsoids are set at the 35% probability level.

comprising carbons C7 and C8 and oriented in such a way that oxygen atom O1 is bound with C8. The C−C bonds of the isoxazoline-bearing pyrrole are considerably longer than those in other pyrroles in line with their single character (Table 1). The macrocyclic ring is slightly saddle-distorted. The mean deviation from the mean plane P_{24} defined by all heavy atoms of the macrocycle is 0.200 Å with N2, C3, C12, C13 localized on one side and C7, C8, C17, C18 on the opposite side of this plane. The dihedral angle between P_{24} and the mean plane of the *confused* pyrrole is only 5.7°; thus, the distortion of the ring has a different character than in the case of **4**. The isoxazoline ring is essentially planar, and the dihedral angle between its mean plane and P_{24} is 70.6°. Because **3a** crystallized as a racemate, the centrosymmetric crystal unit cell contained a pair of enantiomers of opposite configurations on the atoms C7 (*S*/*R*) and C8 (*S*/*R*). The molecules of enantiomers interact mostly by the van der Waals forces but there is also a weak intermolecular hydrogen-bond type interaction between one of the meso-phenyls and the isoxazoline oxygen (C55−H···O1: d_{D-H} = 0.93 Å, d_{H-A} = 2.55 Å d_{D-A} = 3.320(6) Å, D−H···A = 139°). In addition, the distance between chlorine atoms in the Cl2 positions (3.266(9) Å) is shorter than the sum of van der Waals radii (3.50 Å), which suggests an attractive interaction between halogens. The crystal contains no solvent molecules.

The electronic spectra of cycloaddition products **3a** and **4** differ considerably in the positions of major absorption band in the Soret region ($\Delta\lambda$ = 54 nm) with hypsochromic shift observed for carbabacteriochlorin with respect to the carbachlorin (Figure 6). In the case of **3a** the band in this

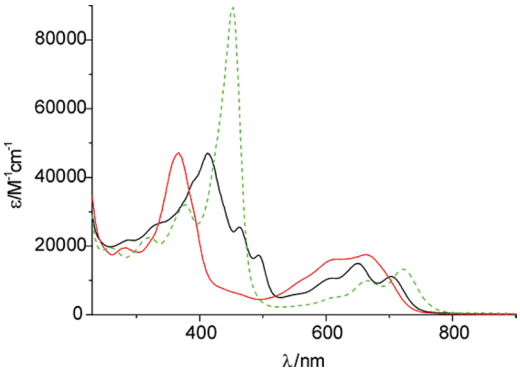

Figure 6. Optical spectra of dichloromethane solutions of **2** (green dashed line), **3a** (black line), and **4** (red line).

region is split into several components which may reflect a lower symmetry of the chromophore than that of the starting porphyrin **2** or the diadduct **4**. For both mono- and diadduct a significant decrease of the Soret band intensity comparing to that of the starting porphyrin is observed along with moderate increase of a major band in the Q region and its blue-shift with respect to **2**.

The mixture of nickel complexes **5a**−**d** was subjected to HPLC on a chiral-phase column. It should be noted that due to the presence of two asymmetric carbon atoms in the carbachlorin ligands each of the complexes **5a**−**d** is represented by two enantiomers, and thus in the mixture there are eight components altogether which are either constitutional isomers or enantiomers. The HPLC profile for this mixture (Figure 7), however, consisted of six peaks indicating severe overlap of some of the bands. ^{1}H NMR of the collected bands revealed that each of the fractions f1−f3 contained one compound, fractions f4 and f5 consisted of three components each, and fraction f6 consisted of one major and one minor component. The UV−vis and NMR spectra of fractions f1 and f2 are identical; thus, these fractions contained enantiomers of one of the constitutional isomers. Comparison of these spectra with that of the mixture and detailed analysis of the low-temperature COSY and NOSY spectra allowed identification of this isomer as **5c** whose population in the mixture was 9%. In the analogous way the complex contained in fraction f3 was identified as the least abundant (7%) **5d**. The fraction f4 consisted of **5d** (second enantiomer), **5a** (first enantiomer), and another isomer whose abundance in the parental mixture was 27%. The second enantiomer of this isomer was a major component of the fraction f5 which contained also about 15% of **5a** and 8%

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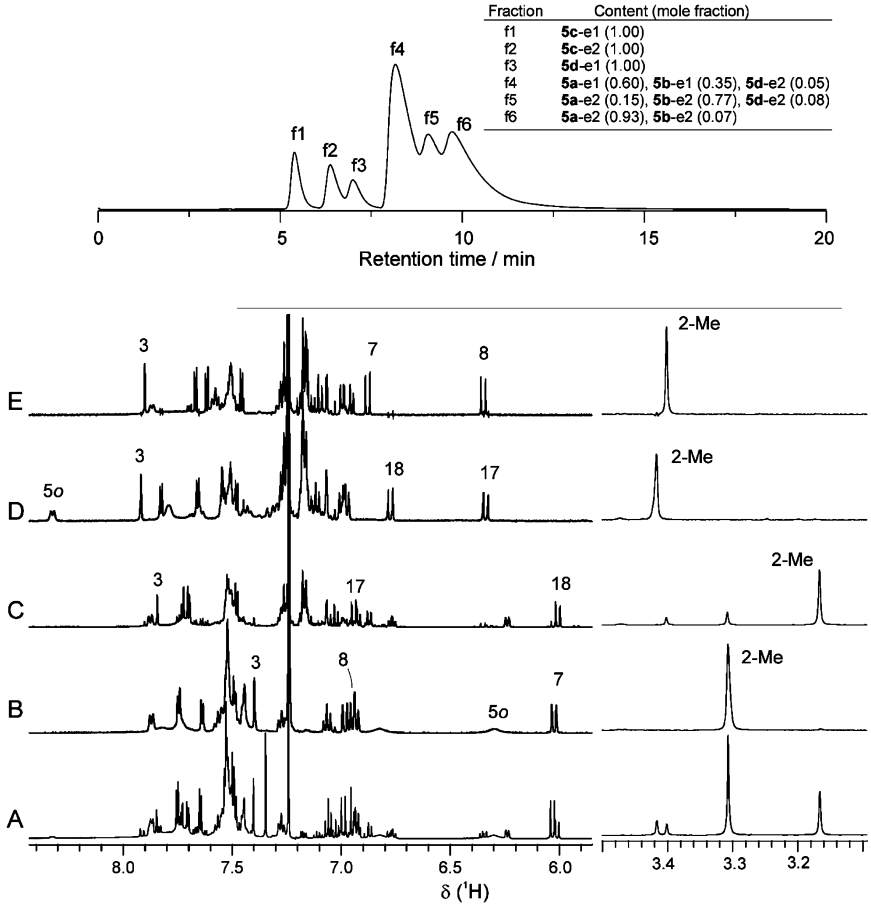

Figure 7. Lower box: ^{1}H NMR spectra (600 MHz, 300 K, $CDCl_3$) of the mixture of complexes **5a**−**d** (A); racemic complex **5a** (B); fraction f5 containing **5b**-e2 as a major component (C); complex **5c**-e1 of fraction f1 (D); **5d**-e1 of fraction f3 (E). Upper box: chiral-phase HPLC profile (injection: 0.5 mg/100 μL; mobile phase: benzene, 1 mL/min; detection at λ = 500 nm) of the mixture **5a**−**d**. In the inset a distribution of components among the fractions f1−f6 is presented. The faster and slower migrating enantiomers of each complex were denoted e1 and e2, respectively.

of **5d** due to a partial overlap of the chromatographic bands. Despite some admixture of the other isomers we could identify the major component in f5 as **5b** on the basis of 2D NMR analysis. The last fraction f6 consisted mainly of second enantiomer of **5a** and about 7% of **5b**.

From the distribution of the complexes in the mixture **5a**−**d** which reflects that of the carbachlorin free base mixture **3a**−**d**, we conclude that a regioselectivity occurred also in the first stage of the cycloaddition reaction since the major product is about twice as prevalent as the second one. Moreover, both most abundant carbachlorin products are precursors of **4** which accounted for the regioselectivity of the formation of the carbabacteriochlorin. Importantly, none of the products involves carbons C12, C13 in the fusion with isoxazoline ring in line with our predictions based on the π-electron delocalization pathway in **2**.

Although all collected fractions are optically active it should be pointed out that only f1, f2 constitute a pair of optical antipodes of **5c**, and for **3d** only one of the enantiomers was isolated. We also resolved enantiomers of **5a**, performing the chiral-phase HPLC for the pure constitutional isomer separated by the flash chromatography or for the mixtures containing only **5a** and **5c** which considerably differ in the retention times (Figure 8). The CD spectra of these pairs of enantiomers (Figure 8) consist of several Cotton effects which are spread over the Soret and Q-band regions. Clearly, the optical activity of these complexes is related with the carbachlorin macrocyclic ring chromophore rather than with that of electronically "isolated" isoxazoline ring whose absorption is expected only in the ultraviolet region. Moreover, the composite character of these CD spectra reflects a low molecular symmetry of the N-confused chlorin complexes. The spectra of similarly high complexity have been observed for monomeric and dimeric nickel(II) complexes of 21-alkylated NCP,[33,46] where apart from the asymmetric character of C21, the substituent on the pyramidal-hybridized internal carbon differentiates enantiotopic faces of the macrocycle and removes the C_s symmetry plane of the prochiral porphyrinoid. A similar source of chirality was observed for N-alkylated enantiotopic porphyrins[47−49] or corroles.[50] In the present case of the N-confused chlorin complexes the optical activity can be considered as a result of plane rather than point chirality (Figure 9). In the case of regular bis(chlorinatozinc) complexes the CD spectra are much less complicated, consisting essentially of two bisignate couplets which are the result of exciton coupling.[51−53]

Demetalation carried out for the separated enantiomers of **5a** resulted in optically active forms of **3a** whose CD spectra (Figure 10) consist of several signals in the UV−vis region with a major peak at the same wavelength (412 nm) as observed for the Soret-type band in the optical spectrum (Figure 6). Also in this case the optical activity is related with the chlorin

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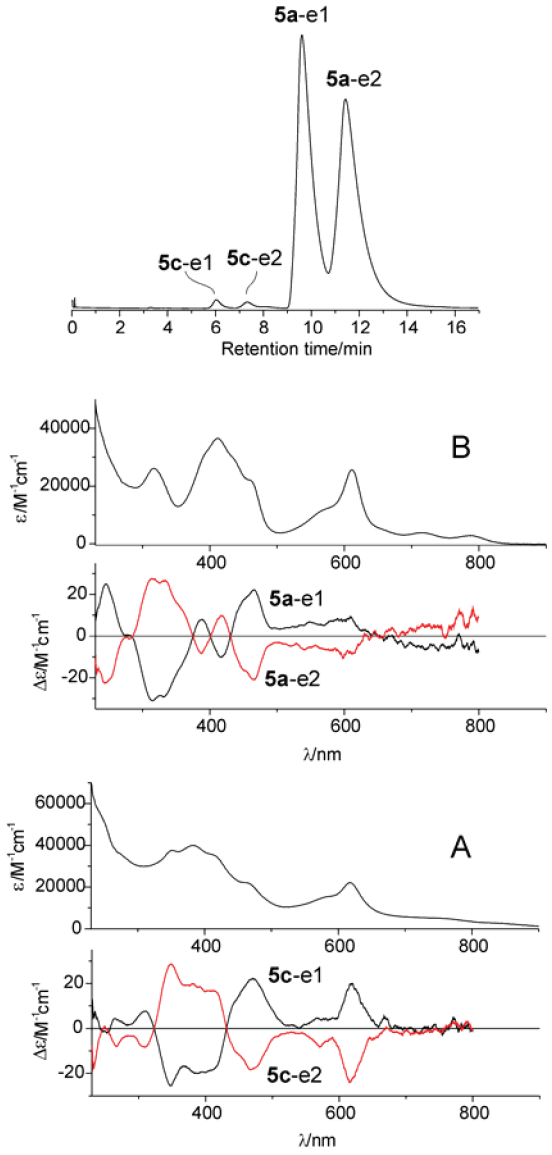

Figure 8. Lower box: optical (upper traces) and CD (lower traces) spectra of enantiomers of **5c** (A) and **5a** (B). Upper box: chiral-phase HPLC profile (injection: 0.5 mg/100 μL, mobile phase: toluene, 1 mL/min, detection at λ = 500 nm) of the mixture **5a** and **5c** (96:4).

chromophore rather than with that of the isoxazoline ring fused to the pyrrole by two sp^3 carbons.

Although the bisadduct, 2-aza-21-carbabacteriochlorin **4** is also chiral, our efforts to separate its enantiomers by HPLC failed despite application of several different chiral stationary phases. Apparently, a handedness of the molecule is too weakly marked which can be accounted for by the presence of two pairs of structurally similar opposite stereogenic centers.

CONCLUSIONS

1,3-Cycloaddition reaction of 2-methylated NCP with dichlorobenzonitrile oxide is highly regio- and stereoselective and constitutes a facile access to a carbabacteriochlorin-type macrocycle which is stable toward autoxidation. The addition proceeds via initial formation of four isomeric monoadducts, and two of them, which together constitute the vast majority of carbachlorin-type products (82%), are precursors of the unique diadduct. The presence of isoxazoline ring fused with one of the pyrrole

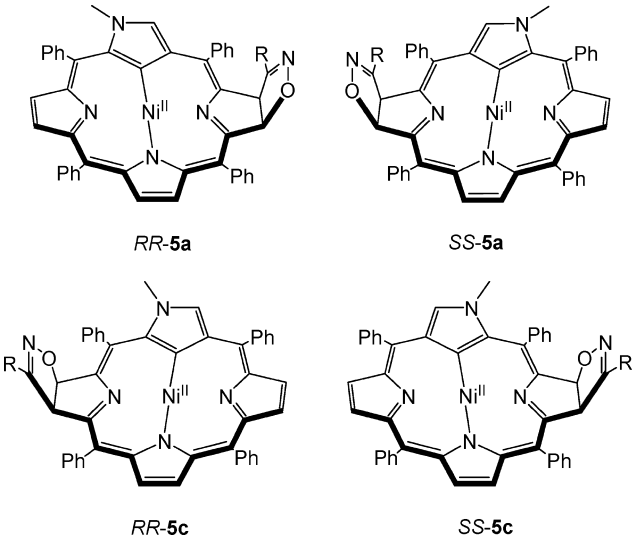

Figure 9. Enantiomers of **5a** and **5c**.

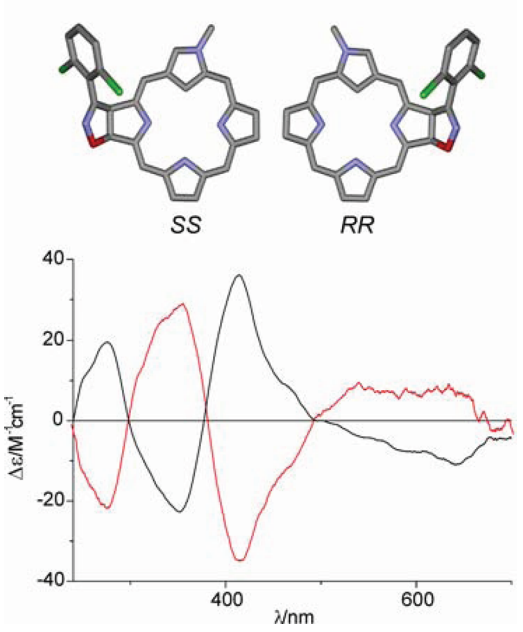

Figure 10. CD spectra of dichloromethane solutions of enantiomers of **3a** obtained by acidic demetalation of the separated optical isomers **5a**-e1 (black trace) and **5a**-e2 (red trace). The skeletons of the enantiomers taken from the crystal structure of **3a** are shown on the top.

differentiates porphyrin's faces leading to intrinsically chiral systems for which enantiomers can be separated in the form of readily formed diamagnetic nickel(II) complexes.

EXPERIMENTAL SECTION

General Methods. Applied dichloromethane was freshly distilled from calcium hydride. Optical and circular dichroism spectra were recorded in dichloromethane. NMR spectra were recorded in $CDCl_3$ and referenced with a signal of residual $CHCl_3$. 2D experiments were performed by means of standard software. The low-temperature NOESY spectra were recorded with 2048 × 512 data blocks and with 400 ms mixing time. Resolution of stereoisomers was performed at room temperature by means of Chirex 3010 analytical column (25 cm length, 4.6 mm i.d.) packed with 5 μm silica gel coated with covalently bound (*S*)-valine and dinitroaniline. The HPLC-grade solvents were applied.

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Syntheses of Precursors. Starting porphyrin **1** and its 2-methylated derivative **2** were synthesized as previously reported.[9,10]

Cycloaddition. General procedure of the 1,3-dipolar cycloaddition of 2,6-dichlorobenzonitrile oxide to 2-methyl-*meso*-tetraphenyl-2-aza-21-carbaporphyrin **2**.

A mixture of **2** (95 mg, 0.15 mmol) and 2,6-dichlorobenzonitrile oxide (189 mg, 1 mmol) were refluxed in 25 mL of dry benzene for 5 h. The solvent was then evaporated and solid residue was dissolved in dichloromethane and subjected to silica gel column chromatography. The polarity of the eluant was increased from 1:100 to 2:100 MeOH/DCM which allows separation of blue bisadduct product **4** (first band, 30 mg, 20%) from green monoadducts **3** (third band, 35 mg, 29%) and unreacted starting **2** (second band, 25 mg).

Selected data for **4**: ^{1}H NMR (500 MHz, $CDCl_3$, 300 K) δ_H = 7.95 (d, ^3J = 7.5 Hz, 2H), 7.75 (b, 1H), 7.58 (t, ^3J = 7.5 Hz, 2H), 7.47 (overlapping multiplets, 6H), 7.38 (b, 1H), 7.21 (dd, ^3J = 8.1 Hz, ^4J = 0.7 Hz, 1H), 7.19 (tt, ^3J = 7.4 Hz, ^4J = 1.5 Hz, 1H), 7.16 (tt, ^3J = 7.4 Hz, ^4J = 1.4 Hz, 1H), 7.11 (dd, ^3J = 8.1 Hz, ^4J = 0.8 Hz, 1H), 7.11 (t, ^3J = 8.1 Hz, 1H), 7.09 (b, 1H), 7.04 (t, ^3J = 8.1 Hz, 1H), 6.96 (dd, ^3J = 5.5 Hz, ^4J = 1.5 Hz, 1H), 6.93 (dd, ^3J = 5.5 Hz, ^4J = 1.4 Hz, 1H), 6.91 (dd, ^3J = 8.0 Hz, ^4J = 0.7 Hz, 1H), 6.84 (dd, ^3J = 8.0 Hz, ^4J = 0.7 Hz, 1H), 6.68 (b, 1H), 6.50 (d, ^3J = 9.6 Hz, 1H), 6.41 (d, ^3J = 9.8 Hz, 1H), 6.17 (d, ^3J = 9.6 Hz, 1H), 5.99 (d, ^3J = 9.8 Hz, 1H), 5.85 (d, ^4J = 1.5 Hz, 1H), 5.82 (b, 1), 2.73 (s, 3H), 2.72 (d, ^4J = 1.5 Hz, 1H); ^{1}H NMR (500 MHz, $CDCl_3$, 228 K) δ_H = 7.93 (d, ^3J = 7.1 Hz, 1H), 7.92 (d, ^3J = 7.5 Hz, 1H), 7.77 (d, ^3J = 7.5 Hz, 1H), 7.66 (d, ^3J = 7.5 Hz, 1H), 7.60 (t, ^3J = 7.5 Hz, 2H), 7.54 (d, ^3J = 7.1 Hz, 1H), 7.52 (d, ^3J = 7.1 Hz, 1H), 7.50 (t, ^3J = 7.1 Hz, 1H), 7.48 (t, ^3J = 7.1 Hz, 1H), 7.38 (t, ^3J = 7.1 Hz, 1H),7.31 (t, ^3J = 7.1 Hz, 1H), 7.21 (t, ^3J = 7.5 Hz, 2H), 7.15 (t, ^3J = 7.5 Hz, 1H), 7.14 (d, ^3J = 8.3 Hz, 1H), 7.08 (t, ^3J = 8.0 Hz, 1H), 7.01 (dd, ^3J = 5.5 Hz, ^4J = 1.2 Hz, 1H), 6.97 (dd, ^3J = 5.5 Hz, ^4J = 1.2 Hz, 1H), 6.88 (d, ^3J = 8.4 Hz, 1H), 6.85 (t, ^3J = 7.6 Hz, 1H), 6.83 (t, ^3J = 7.6 Hz, 1H), 6.82 (d, ^3J = 8.4 Hz, 1H), 6.81(t, ^3J = 7.6 Hz, 1H), 6.71 (d, ^3J = 7.6 Hz, 1H), 6.66 (d, ^3J = 7.6 Hz, 1H), 6.61 (d, ^3J = 9.7 Hz, 1H), 6.51 (d, ^3J = 9.7 Hz, 1H), 6.24 (d, ^3J = 9.7 Hz, 1H), 6.08 (d, ^3J = 9.7 Hz, 1H), 5.90 (s, 1H), 5.48 (s, 1H), 2.72 (s, 3H), 2.33 (s, 1H); ^{13}C NMR (126 MHz, $CDCl_3$, 300 K) δ_C = 168.4, 166.8, 153.1, 152.7, 150.0, 148.1, 146.9, 146.1, 141.0, 139.4, 139.3, 139.1, 136.2, 135.9, 135.1, 134.8, 134.1, 134.0, 131.4, 130.2, 129.2, 128.75, 128.68, 128.5, 128.3, 128.1, 128.0, 127.9, 127.8, 127.7, 127.62, 127.56, 127.1, 126.7, 126.4, 123.4, 123.4, 121.8, 114.4, 113.3, 99.2, 89.2, 89.0, 55.9, 55.6, 36.5; UV−vis (CH_2Cl_2, 298 K) λ/nm (ε/M^{-1} cm^{-1}) = 282 (19500), 366 (47000), 462 (sh), 556 (sh), 611 (16100), 663(17500); HRMS (ESI-TOF) m/z = 1003.1881 (obsd), 1003.1888 (calcd for $C_{59}H_{39}Cl_4N_6O_2$, $[M + H]^+$).

Metalation of 3a−d. Solution containing mixture of monoadducts **3a−d** (30 mg, 0.0367 mmol) dissolved in benzene (20 mL) and nickel(II) acetate dihydrate (80 mg, 0.37 mmol) in ethanol (10 mL) was heated under reflux for 4 h under nitrogen. After that time, the solvents were removed and the solid residue was dissolved in dichloromethane, filtered, and passed down the SiO_2 column with dichloromethane as a mobile phase. The solvent volume was reduced, and complexes **5a−d** were precipitated by addition of hexane and collected by filtration. Yield of metalation: 29.8 mg (93%).

Separation of Isomers 5a−d. The mixture of complexes in toluene solution (20 mg) was subjected to flash chromatography on a 15 cm column filled with fine silica gel particles (10−40 μm diameter). A nitrogen gas overpressure of 2 bar was applied to force elution. The collectors were changed after every 2 mL of discharge. The content of each fraction was examined by ^{1}H NMR after the eluant was evaporated. The early fractions containing only **5a** were combined and evaporated, and the complex was crystallized from chloroform/hexane mixture. Yield: 5 mg.

A sample of 10 mg of the mixture of complexes **5a−d** was subjected to separation on a chiral-phase HPLC column with benzene as a mobile phase. The separation was carried out by performing a series of 20 consecutive 0.1 mL injections and collecting fractions which corresponded with each peak on the chromatograms.

Selected data for **5a**: ^{1}H NMR (600 MHz, $CDCl_3$, 300 K) δ_H = 7.87 (d, ^3J = 6.9 Hz, 1H), 7.82 (b, 1H), 7.74 (d, ^3J = 5.2 Hz, 1H), 7.73 (b, 1H), 7.63 (d, ^3J = 4.6 Hz, 1H), 7.56 (t, ^3J = 6.9 Hz, 1H), 7.53 (d, ^3J = 4.6 Hz, 1H), 7.52−7.50 (overlapping multiplets, 3H), 7.49 (d, ^3J = 5.2 Hz, 1H), 7.40 (t, ^3J = 6.9 Hz, 1H), 7.27 (tt, ^3J = 7.5 Hz, ^4J = 1.0 Hz, 1H), 7.07 (t, ^3J = 7.8 Hz, 1H), 6.98 (d, ^3J = 10.4 Hz, 1H), 6.95 (dd, ^3J = 7.9 Hz, ^4J = 0.9 Hz, 1H), 6.93 (dd, ^3J = 7.9 Hz, ^4J = 0.9 Hz, 1H), 6.83 (b, 1H), 6.30 (b, 1H), 6.02 (d, ^3J = 10.4 Hz, 1H), 3.31 (s, 3H); ^{1}H NMR (600 MHz, $CDCl_3$, 213 K) δ_H = 8.34 (d, ^3J = 7.3 Hz, 1H), 7.96 (d, ^3J = 7.0 Hz, 1H), 7.89 (d, ^3J = 7.4 Hz, 1H), 7.86 (d, ^3J = 7.7 Hz, 1H), 7.80 (d, ^3J = 4.8 Hz, 1H), 7.72 (d, ^3J = 4.8 Hz, 1H), 7.70 (t, ^3J = 7.7 Hz, 1H), 7.59 (t, ^3J = 6.7 Hz, 1H), 7.58 (t, ^3J = 6.7 Hz, 1H), 7.57 (d, ^3J = 4.8 Hz, 1H), 7.55 (t, ^3J = 6.7 Hz, 1H), 7.54 (t, ^3J = 6.7 Hz, 1H), 7.53 (d, ^3J = 4.8 Hz, 1H), 7.51 (d, ^3J = 7.6 Hz, 1H), 7.49 (s, 1H), 7.45 (t, ^3J = 7.6 Hz, 2H), 7.41 (t, ^3J = 6.7 Hz, 1H), 7.37 (d, ^3J = 7.6 Hz, 1H), 7.27 (t, ^3J = 7.5 Hz, 1H), 7.23 (d, ^3J = 7.6 Hz, 1H), 7.09 (t, ^3J = 8.1 Hz, 1H), 7.07 (d, ^3J = 10.3 Hz, 1H), 6.91 (d, ^3J = 8.1 Hz, 1H), 6.90 (d, ^3J = 8.2 Hz, 1H), 6.79 (t, ^3J = 7.3 Hz, 1H), 6.22 (d, ^3J = 7.4 Hz, 1H), 6.11 (d, ^3J = 10.3 Hz, 1H), 3.31 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$, 300 K) δ_C = 157.9, 154.0, 153.1, 150.7, 145.3, 145.2, 145.0, 140.6, 139.5, 139.2, 139.1, 139.0, 136.6, 135.4, 134.6, 133.1, 132.8, 131.2, 131.1, 131.0, 130.8, 130.3, 128.3, 128.0, 127.7, 127.6, 127.5, 127.44, 127.38, 127.35, 127.2, 127.1, 127.0, 126.6, 124.5, 121.1, 120.1, 112.6, 89.1, 54.4, 39.7; UV−vis (CH_2Cl_2, 298 K) λ/nm (ε/M^{-1} cm^{-1}) = 317 (26100), 396 (sh), 412 (36500), 432 (sh), 440 (sh), 460 (sh), 566 (sh), 610 (25600), 654 (sh), 715 (3800), 787 (2900); HRMS (ESI-TOF) m/z = 872.1497 (obsd), 872.1493 (calcd for $C_{52}H_{34}Cl_2N_5NiO$, $[M + H]^+$).

Selected data for **5b**: ^{1}H NMR (600 MHz, $CDCl_3$, 300 K) δ_H = 7.87 (dt, ^3J = 7.8 Hz, ^4J = 1.5 Hz 1H), 7.84 (q, ^4J = 0.6 Hz, 1H), 7.73 (d, ^3J = 5.0 Hz, 1H), 7.698 (d, ^3J = 4.9 Hz, 1H), 7.697 (d, ^3J = 5.0 Hz, 1H), 7.54−7.49 (overlapping multiplets, 6H), 7.48 (d, ^3J = 4.9 Hz, 1H), 7.27 (t, ^3J = 7.4 Hz, 1H), 7.17 (t, ^3J = 7.6 Hz, 1H), 7.16 (t, ^3J = 6.2 Hz, 1H), 7.03 (t, ^3J = 7.9 Hz, 1H), 6.94 (d, ^3J = 10.1 Hz, 1H), 6.92 (dd, ^3J = 8.0 Hz, ^4J = 1.0 Hz, 1H), 6.87 (dd, ^3J = 8.0 Hz, ^4J = 1.0 Hz, 1H), 6.76 (tdd, ^3J = 7.5 Hz, ^4J = 1.5 Hz, ^5J = 0.5 Hz, 1H), 6.24 (dtt, ^3J = 7.6 Hz, ^4J = 1.3 Hz, ^5J = 0.6 Hz, 1H), 6.01 (d, ^3J = 10.1 Hz, 1H), 3.17 (d, ^4J = 0.6 Hz, 3H); ^{1}H NMR (600 MHz, $CDCl_3$, 213 K) δ_H = 8.35 (d, ^3J = 7.6 Hz, 1H), 8.01 (s, 1H), 7.97 (d, ^3J = 7.6 Hz, 1H), 7.95 (d, ^3J = 7.4 Hz, 1H), 7.90 (d, ^3J = 7.8 Hz, 1H), 7.78 (d, ^3J = 4.1 Hz, 1H), 7.74 (d, ^3J = 4.9 Hz, 1H), 7.70 (t, ^3J = 8.0 Hz, 1H), 7.63−7.42 (overlapping multiplets, 7H), 7.40 (t, ^3J = 7.4 Hz, 1H), 7.32 (t, ^3J = 7.6 Hz, 1H), 7.27 (t, ^3J = 7.8 Hz, 1H), 7.26 (d, ^3J = 7.5 Hz, 1H), 7.18 (d, ^3J = 7.5 Hz, 1H), 7.07 (t, ^3J = 7.5 Hz, 1H), 7.06 (t, ^3J = 8.2 Hz, 1H), 7.04 (d, ^3J = 10.3 Hz, 1H), 6.89 (d, ^3J = 8.2 Hz, 1H), 6.86 (d, ^3J = 7.8 Hz, 1H), 6.72 (t, ^3J = 7.7 Hz, 1H), 6.17 (d, ^3J = 7.5 Hz, 1H), 6.10 (d, ^3J = 10.3 Hz, 1H), 3.20 (s, 3H); UV−vis (CH_2Cl_2, 298 K) λ/nm (ε/M^{-1} cm^{-1}) = 244 (sh), 321 (35000), 340 (sh), 392 (43200), 412 (sh), 464 (sh), 567 (sh), 616 (27200), 651 (sh), 834 (sh); HRMS (ESI-TOF) m/z = 872.1498 (obsd), 872.1493 (calcd for $C_{52}H_{34}Cl_2N_5NiO$, $[M + H]^+$).

Selected data for **5c**: ^{1}H NMR (600 MHz, $CDCl_3$, 300 K) δ_H = 8.32 (d, ^3J = 6.9 Hz, 1H), 7.92 (s, 1H), 7.82 (d, ^3J = 4.9 Hz, 1H), 7.79 (b, 2H), 7.66 (d, ^3J = 4.9 Hz, 1H), 7.64 (t, ^3J = 7.6 Hz, 1H), 7.56−7.49 (overlapping multiplets, 5H), 7.48 (d, ^3J = 5.0 Hz, 1H), 7.43 (t, ^3J = 7.3 Hz, 1H), 7.30 (d, ^3J = 7.5 Hz, 1H), 7.27 (t, ^3J = 7.5 Hz, 1H), 7.17 (d, ^3J = 5.0 Hz, 1H), 7.16 (t, ^3J = 7.6 Hz, 1H), 7.11 (d, ^3J = 8.0 Hz, 1H), 7.00 (dd, ^3J = 8.0 Hz, ^4J = 1.0 Hz, 1H), 6.97 (dd, ^3J = 8.0 Hz, ^4J = 1.0 Hz, 1H), 6.77 (d, ^3J = 10.6 Hz, 1H), 6.33 (d, ^3J = 10.6 Hz, 1H), 3.41 (s, 3H); ^{1}H NMR (600 MHz, $CDCl_3$, 213 K) δ_H = 8.28 (d, ^3J = 7.7 Hz, 1H), 7.97 (s, 1H), 7.95 (d, ^3J = 6.8 Hz, 1H), 7.93 (d, ^3J = 4.9 Hz, 1H), 7.78 (d, ^3J = 7.4 Hz, 1H), 7.71 (d, ^3J = 4.9 Hz, 1H), 7.68 (t, ^3J = 7.8 Hz, 1H), 7.66 (d, ^3J = 7.7 Hz, 1H), 7.59 (t, ^3J = 7.5 Hz, 2H), 7.57 (d, ^3J = 7.3 Hz, 1H), 7.55 (t, ^3J = 7.8 Hz, 2H), 7.54 (t, ^3J = 7.8 Hz, 2H), 7.51 (d, ^3J = 4.9 Hz, 1H), 7.48 (t, ^3J = 7.9 Hz, 1H), 7.45 (t, ^3J = 7.8 Hz, 1H), 7.43 (t, ^3J = 7.9 Hz, 1H), 7.37 (d, ^3J = 7.5 Hz, 1H), 7.28 (t, ^3J = 7.5 Hz, 1H), 7.18 (d, ^3J = 4.8 Hz, 1H), 7.14 (t, ^3J = 7.9 Hz, 1H), 6.98 (d, ^3J = 8.4 Hz, 1H), 6.96 (d, ^3J = 8.1 Hz, 1H), 6.83(d, ^3J = 10.7 Hz, 1H), 6.81 (t, ^3J = 7.6 Hz, 1H), 6.42 (d, ^3J = 10.7 Hz, 1H), 6.35 (d, ^3J = 7.4 Hz, 1H), 3.41 (s, 3H); UV−vis (CH_2Cl_2, 298 K) λ/nm (ε/M^{-1} cm^{-1}) = 252 (sh), 279 (sh), 351 (37600), 383 (39900), 416 (sh), 466 (sh), 577 (sh), 6186 (22000), 753 (sh), 844

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(sh); HRMS (ESI-TOF) m/z = 872.1474 (obsd), 872.1493 (calcd for $C_{52}H_{34}Cl_2N_5NiO$, $[M + H]^+$).

Selected data for **5d**: ^{1}H NMR (600 MHz, $CDCl_3$, 300 K) δ_H = 7.94 (s, 1H), 7.90 (d, ^3J = 6.9 Hz, 1H), 7.79 (b, 2H), 7.70 (d, ^3J = 5.0 Hz, 1H), 7.65 (d, ^3J = 5.0 Hz, 1H), 7.61 (t, ^3J = 8.1 Hz, 2H), 7.59−7.50 (overlapping multiplets, 4H), 7.49 (d, ^3J = 5.0 Hz, 1H), 7.31 (t, ^3J = 7.5 Hz, 1H), 7.19 (d, ^3J = 5.0 Hz, 1H), 7.14 (t, ^3J = 8.0 Hz, 1H), 7.03, 6.98 (dd, ^3J = 8.0 Hz, ^4J = 1.0 Hz, 1H), 6.91 (d, ^3J = 10.4 Hz, 1H), 6.38 (d, ^3J = 10.4 Hz, 1H), 3.44 (s, 3H). ^{1}H NMR (600 MHz, $CDCl_3$, 213 K) δ_H = 8.23 (d, ^3J = 7.6 Hz, 1H), 7.99 (s, 1H), 7.96 (d, ^3J = 7.2 Hz, 1H), 7.92 (d, ^3J = 7.2 Hz, 1H), 7.81 (d, ^3J = 7.6 Hz, 1H), 7.73 (d, ^3J = 5.0 Hz, 1H), 7.70 (d, ^3J = 4.7 Hz, 1H), 7.66 (t, ^3J = 7.7 Hz, 1H), 7.62 (t, ^3J = 7.5 Hz, 1H), 7.58 (t, ^3J = 7.3 Hz, 1H), 7.55 (d, ^3J = 7.7 Hz, 1H), 7.53 (t, ^3J = 6.9 Hz, 1H), 7.51 (t, ^3J = 8.0 Hz, 1H), 7.50 (t, ^3J = 7.6 Hz, 1H), 7.48 (t, ^3J = 7.8 Hz, 1H), 7.46 (d, ^3J = 4.7 Hz, 1H), 7.46 (d, ^3J = 8.0 Hz, 1H), 7.44 (t, ^3J = 7.8 Hz, 1H), 7.28 (d, ^3J = 8.0 Hz, 1H), 7.15 (d, ^3J = 5.0 Hz, 1H), 7.14 (t, ^3J = 8.0 Hz, 1H), 6.98 (d, ^3J = 8,0 Hz, 1H), 6.96 (d, ^3J = 10.6 Hz, 1H), 6.94 (d, ^3J = 8,0 Hz, 1H), 6.79 (t, ^3J = 7.8 Hz, 1H), 6.45 (d, ^3J = 10.6 Hz, 1H), 6.30 (d, ^3J = 8.0 Hz, 1H), 3.38 (s, 3H); UV−vis (CH_2Cl_2, 298 K) λ/nm (ε/M^{-1} cm^{-1}) = 248 (sh), 322 (28700), 392 (sh), 418 (37600), 462 (sh), 571 (sh), 616 (26200), 725 (3900), 792 (3000); HRMS (ESI-TOF) m/z = 872.1476 (obsd), 872.1493 (calcd for $C_{52}H_{34}Cl_2N_5NiO$, $[M + H]^+$).

Demetalation of 5a. A sample of 3 mg of **5a** was dissolved in 5 mL of dichloromethane and shaken with 1 mL of concentrated hydrochloric acid for 10 min. After that time, the solution of resulting **3a** was washed with several portions of water, dried with anhydrous potassium carbonate, filtered, and crystallized by addition of hexane. Yield: 2.0 mg (85%).

Selected data for **3a**: ^{1}H NMR (600 MHz, $CDCl_3$, 300 K) δ_H = 8.11 (dt, ^3J = 7.8 Hz, ^4J = 1.5 Hz, 1H), 7.87 (m, 2H), 7.73 (m, 2H), 7.629 (d, ^3J = 4.5 Hz, 1H), 7.626 (t, ^3J = 7.4 Hz, 1H), 7.58 (m, 2H), 7.55−7.50 (overlapping multiplets, 6H), 7.49 (d, ^3J = 5.5 Hz, 1H), 7.49 (t, ^3J = 7.2 Hz, 1H), 7.44 (t, ^3J = 7.3 Hz, 1H), 7.259 (d, ^3J = 5.5 Hz, 1H), 7.258 (d, ^3J = 4.5 Hz, 1H), 7.07 (m ABX, 2H), 6.92 (dd, ^3J = 7.2 Hz, ^4J = 1.9 Hz, 1H), 6.71 (d, ^3J = 9.97 Hz, 1H), 6.48 (d, ^4J = 1.7 Hz, 1H), 6.27 (d, ^3J = 9.97 Hz, 1H), 4.48 (b, 1H), 3.11 (s, 3H), 1.74 (d, ^4J = 1.7 Hz, 1H); ^{1}H NMR (600 MHz, $CDCl_3$, 213 K) δ_H = 8.10 (d, ^3J = 7.5 Hz, 1H), 7.96 (d, ^3J = 6.9 Hz, 1H), 7.86(d, ^3J = 7.2 Hz, 1H), 7.82 (d, ^3J = 7.5 Hz, 1H), 7.75 (d, ^3J = 7.5 Hz, 1H), 7.74 (d, ^3J = 7.3 Hz, 1H), 7.70 (d, ^3J = 4.6 Hz, 1H), 7.66 (t, ^3J = 7.5 Hz, 1H), 7.64 (d, ^3J = 6.9 Hz, 1H), 7.61−7.53 (overlapping multiplets, 7H), 7.51 (t, ^3J = 7.2 Hz, 1H), 7.38 (t, ^3J = 7.3 Hz, 1H), 7.32 (d, ^3J = 4.5 Hz, 1H), 7.30 (dd, ^3J = 5.4 Hz, ^4J = 1.7 Hz, 1H), 7.26 (t, ^3J = 7.3 Hz, 1H), 7.11 (t, ^3J = 7.9 Hz, 1H), 7.06 (d, ^3J = 7.9 Hz, 1H), 6.91 (t, ^3J = 7.9 Hz, 1H), 6.88 (d, ^3J = 7.6 Hz, 1H), 6.82 (d, ^3J = 9.8 Hz, 1H), 6.72 (d, ^3J = 7.6 Hz, 1H), 6.53 (d, ^4J = 1.4 Hz, 1H), 6.38 (d, ^3J = 9.8 Hz, 1H), 4.15 (t, ^4J = 1.8 Hz, 1H), 3.11 (s, 3H), 1.32 (d, ^4J = 1.4 Hz, 1H); UV−vis (CH_2Cl_2, 298 K) λ/nm (ε/M^{-1} cm^{-1}) = 287 (21700), 326 (sh), 389 (sh), 412 (47000), 463 (25500), 494 (17300), 547 (sh), 609 (10600), 650 (15000), 703 (11100); HRMS (ESI-TOF) m/z = 816.2285 (obsd), 816.2296 (calcd for $C_{52}H_{36}Cl_2N_5O$, $[M + H]^+$).

Crystallographic Data. X-ray quality crystals of **3a** were obtained by slow diffusion of dichloromethane solution of **3a** into hexane at room temperature. Crystal data for **3a**: $C_{52}H_{35}Cl_2N_5Ni_{0.05}$, M_r = 819.69, T = 100(2) K, Mo Kα radiation, triclinic, space group P-1, a = 12.160(8) Å, b = 13.231(9) Å, c = 13.696(1) Å, α = 72.11(7)°, β = 68.34(7)°, γ = 75.15(6)°, V = 1923.4(2) Å^3, Z = 2, D_c = 1.415 Mg m^{-3}, λ = 0.71073 Å, μ = 0.24 mm^{-1}, diffractometer with CCD detector, 2.58 ≤ θ ≤ 25.0°, 14414 collected reflections, 6532 independent reflections, 542 parameters, $R_1(F)$ = 0.065, $wR_2(F^2)$ = 0.166, S = 0.82, largest difference peak and hole 0.71 and −0.33 e·Å^{-3}. The structure was solved by direct methods using the SHELXS program.[54] All non-hydrogen atoms were refined anisotropically by full matrix least-squares with SHELXL-97.[54] All H atoms were placed in a calculated position and refined as the riding model with Uiso(H) = 1.2Ueq(C). The presence of 5% of nickel atom in the crystal lattice can be accounted for by cocrystallization of a residual nickel complex **5a** that apparently survived acidic demetalation and was present in the crystal's mother liquor.

X-ray quality crystals of **4** were obtained by slow diffusion of chloroform solution of **4** into hexane. Crystal data for **4**: $C_{59}H_{37}Cl_4N_6O_2{\cdot}1.5CHCl_3{\cdot}0.5$(*n*-hexane), M_r = 1225.88, T = 100(2) K, Mo Kα radiation, monoclinic, space group $P2_1/c$, a = 12.190(5) Å, b = 27.885(10) Å, c = 17.484 (7) Å, β = 102.23(4)°, V = 5808.2(4) Å^3, Z = 4, D_c = 1.402 Mg m^{-3}, λ = 0.71073 Å, μ = 0.46 mm^{-1}, diffractometer κ-geometry with CCD detector, 3.0 ≤ θ ≤ 25.0°, 35944 collected reflections, 10211 independent reflections, 748 parameters, $R_1(F)$ = 0.063, $wR_2(F^2)$ = 0.163, S = 0.94, largest difference peak and hole 1.11 and −0.76 e·Å^{-3}. The structure was solved by direct methods using the SHELXS program.[54] All non-hydrogen atoms were refined anisotropically by full matrix least-squares with SHELXL-97.[54] All H atoms were placed in a calculated position and refined as the riding model with Uiso(H) = 1.2Ueq(C).

■ ASSOCIATED CONTENT

Supporting Information

Crystallographic data (CIF), 1D and 2D NMR, and UV−vis spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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