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Regioselective Amination of Carbaporpholactone and *N*-Confused Porphyrin

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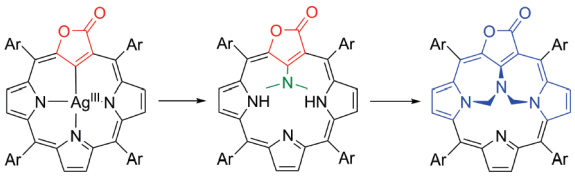

An efficient route to the direct amination at the inner carbon of carbaporpholactone is reported. A regioselectivity of substitution is enforced by activation of the embedded furanone fragment due to coordination of the highly oxidized silver(III) cation. A stepwise oxidation of the dimethylamine derivative leads to the internally bridged carbaporpholactones which contain respectively [5.7.5] tricyclic or [5.7.5.7.5] pentacyclic rings. The analogous reactivity of *N*-confused porhyrin has been also explored.

Introduction

Carbaporphyrinoids are porphyrin (heteroporphyrin) analogues that possess at least one CH unit replacing pyrrolic nitrogen in the coordination core.[1a−f] The unique organometallic chemistry is developed in the restricted geometry of the coordination core imposed by carbaporphyrinoids. Such an environment allows us to address several fundamental questions of interactions which involve a metal ion and a C−H fragment affording a whole spectrum of situations including such extremes as a covalent metal−carbon bond or a weak metal−π interaction.[2a−d]

The inherent reactivity of the embedded ring of carbaporphyrinoids creates intriguing perspectives for construction of derivatives with a modified functionality of the porphyrin interior. The internal carbon, often found susceptible to substitution reactions, can be modified by alkylations,[3a−d] halogenations,[4a−c] nitration,[5]acetoxylation,[6] C-cyanide addition,[7] oxygen insertion,[8a,b] sulfur insertion,[9] formation of ketal,[10] hydroxylation,[8b,11,12] or pyridination.[13]

Some of the above listed reactions are simple electrophilic substitutions, while in other cases an auxiliary oxidant is required.[7,8,10,13−15]

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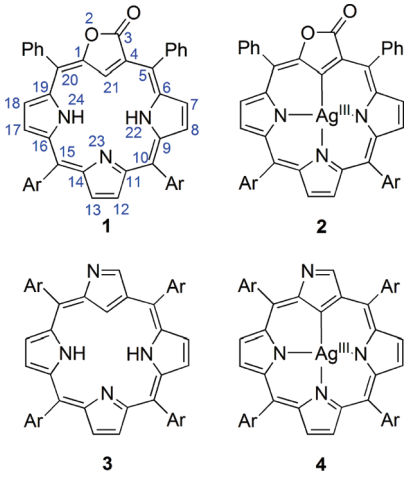
CHART 1

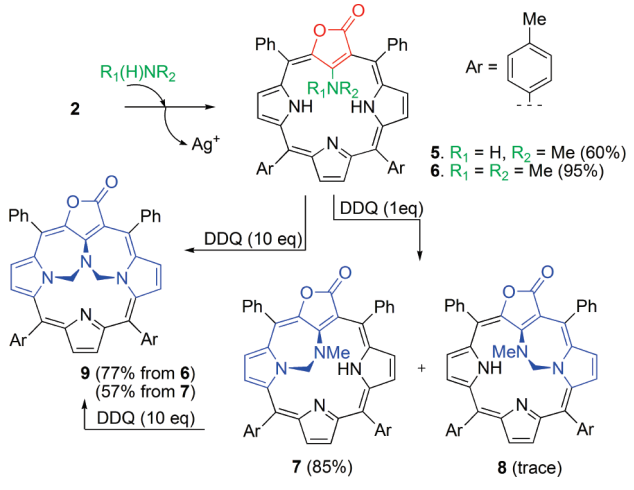


Here we report on the amination of carbaporpholactone **1**, i.e. the carbaporphyrinoid which is derived from *O*-confused oxaporphyrin[16] and *N*-confused porphyrin **3** (Chart 1).[1a,b] Functionalization takes place at the inner C(21) carbon atom of **1** or **3** yielding the respective alkylamino derivatives. A subsequent oxidative transformation involving the *N*-alkyl substituent leads to *N*-fused macrocycles.

Results and Discussion

Treatment of silver(III) carbaporpholactone **2** dissolved in toluene with methylamine or dimethylamine solution in ethanol (298 K) resulted in the prompt formation of carbaporpholactone derivatives **5** and **6** substituted with alkyl amine at the C(21) position indicated by a solution color change from red to green. The substitution has been accompanied by the extrusion of silver(I) formed from the initially coordinated silver(III) cation. Significantly the parallel experiment demonstrated that the free carbaporpholactone **1** is inert toward alkyl amine(s) in analogous conditions pointing out that the coordination of a highly oxidized metal cation is a prerequisite factor of the amination, as recently reported for the regioselective reactivity of **2** toward potassium phosphide.[15] The synthetic work is summarized in Scheme 1.

SCHEME 1. Synthesis of Inner *N*-Alkylated Carbaporpholactone Derivatives



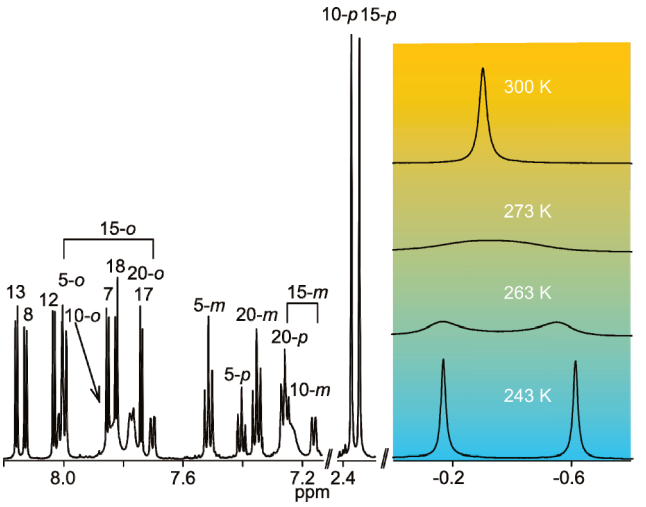


FIGURE 1. ^{1}H NMR spectra of **6** (toluene-d_8, 298 K). Resonance labels follow systematic position numbering (Chart 1). Inset presents the upfield region in different temperatures that show a dynamic process observed for the inner substituent.

The overall reaction for dimethylamine as a substrate may be written as follows:

$$\mathbf{2} + Me_2NH + EtOH \rightarrow \mathbf{6} + Ag^+ + EtO^-$$

The ^{1}H NMR spectra of **5** and **6** confirm the internal substitution of the lactone−furanone moiety (Figure 1). The signal pattern of the peripheral protons (three β-pyrrole AB systems) found in **1** or **2** is preserved in **5** and **6**. The signal of H(21) is replaced by upfield located methyl resonances readily related to the 21-*N*-alkyl substituent(s). The complete assignment of whole ^{1}H NMR spectra for **5** and **6** (Figure 1) has been obtained by means of 2D ^{1}H NMR COSY and NOESY experiments using the unique NOE correlation between H(7) and *ortho*-H(5-phenyl) as a starting point. The purposely synthesized analogue of **1**, i.e. 5,10,15-tritolyl-20-phenylcarbaporpholactone (**1a**), introduces the necessary differentiation of *meso*-substituents at 5 and 20 positions. In the course of analysis we have assumed that the furanone moiety remains canted with respect to the tripyrrolic plane due to the steric hindrance imposed by C(21) substitution. Such a structural factor imposes in-plane chirality reflecting the unsymmetrical substitution at β-positions and renders two, unequivalent opposite sides of the macrocycle. Accordingly, the nitrogen substituents are diastereotopically differentiated as clearly observed for **6** at 243 K (Figure 1) although a single methyl resonance has been detected at 298 K. The equivalence of two methyl resonances at 293 K is readily explained assuming that the dynamic process, which combines an amine nitrogen inversion and a rotation around the C(21)−N bond (Scheme 2), is rapid on the ^{1}H NMR scale.

The line shape analysis of the dynamic N−Me_2 system has been carried out. The spectra were analyzed according to the process defined in Scheme 2 in the 227−318 K temperature range with one rate constant k. Activation parameters were obtained from the least-squares fits of the rate constants to the Arhenius and Eyring equations (see Supporting

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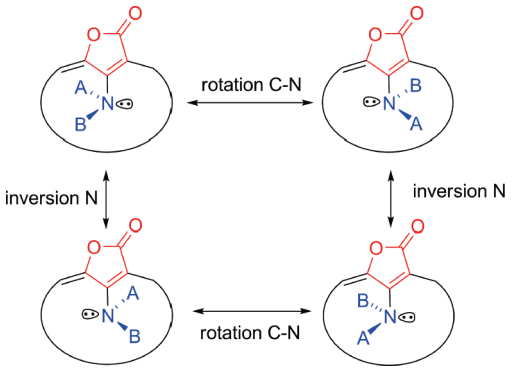
SCHEME 2. Exchange of *N*-Methyls



Information). They equal $E_a = 35.0 \pm 0.5$ kJ/mol (8.4 ± 0.1 kcal/mol), $\Delta H^{\ddagger} = 63.9 \pm 0.9$ kJ/mol, and $\Delta S^{\ddagger} = 44.7 \pm 3.5$ J/K. In contrast to **6**, a single *N*-methyl resonance of **5** has been observed in the whole investigated temperature range. Nevertheless the gradual increase in the line width, detected once the temperature was systematically lowered, requires the analogue sequence of conformational events such as those determined for **6**. Evidently the replacement of methyl by hydrogen facilitates the conformational exchange lowering markedly the collapsing temperature.

Two well-separated *ortho*- and *meta*-resonances of 15-aryl but single sets for 5,10,20-aryls of **5** and **6** have been detected at 298 K (Figure 1). This observation confirms the nonplanarity of the aminated carbaporpholacton macrocycles. Two sides of **5** or **6** remain unequivalent as clearly revealed because of the slow rotation of 15-aryl rings around the $C_{meso}-C_{ipso}$ bond.

A mechanism of amination in which the Ag(III) species undergoes reversible axial coordination of amine followed by a reductive elimination step to yield, after extrusion of Ag(I), the aminated species **5** or **6** can be envisaged. The presence of silver(I) in the reaction products has been analytically confirmed. The detected regioselectivity is unlikely for a radical intermediate but can be readily accounted assuming that the substitution proceeds through a highly oxidized silver complex. In fact the analogous regioselective mechanism of phosphanylation of **2** produced a diphenylphosphoryl-carbaporpholactone hybrid.[15] Significantly the intramolecular oxidation of silver(III) 3-hydroxy *O*-confused porphyrin derivatives accompanied by the silver(I) extrusion which involved the external C(3) position has been documented as well.[16]

The placement of the dimethylamine moiety in the cavity of the carbaporpholactone seems to be a factor in the remarkable fusion reactions discovered for **6**, resulting in formation of the seven-membered ring(s). Thus the addition of a proper amount of DDQ to the solution of **6** results in the formation of the N(amine)$-CH_2-$N(pyrrole) bridged species **7**, **8**, or **9**. The analogous compounds have been originally identified as the side products of the reaction between **2** and dimethylamine.

The methylene linkers of **7** and **9** allowed preservation of the symmetry and electronic structure of the basic chromophore contained in maternal **5** as revealed by noteworthy similarities of the UV−vis electronic spectra (Figure 2). The detected differences are related to the replacement

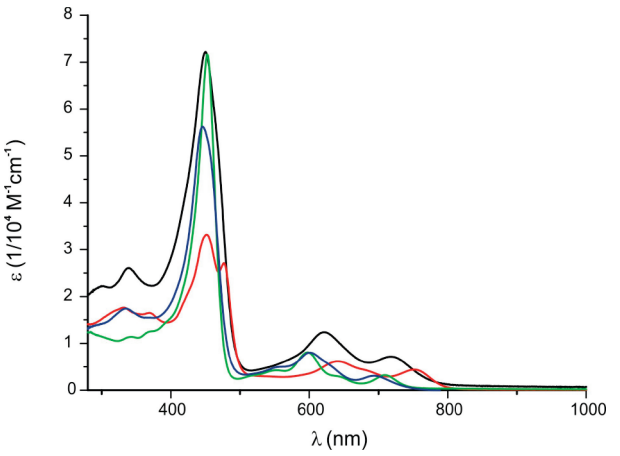


FIGURE 2. UV−vis electronic spectra of **5** (blue) in benzene and **6** (black), **7** (green), and **9** (red) in dichloromethane.

of NH fragments by $N-CH_2$ ones. The structures of compound **7** and **9** were determined by careful analysis of ^1H and ^{13}C NMR data (Figure 3). In particular, the transformation of *N*-methyls into the bridging methylene results in the rise of characteristically upfield shifted AX type patterns accompanied by a disappearance of the appropriate NH resonance. Actually **8**, which has been solely spectroscopically identified, demonstrated the characteristic set of upfield resonances (Me −2.34 ppm,

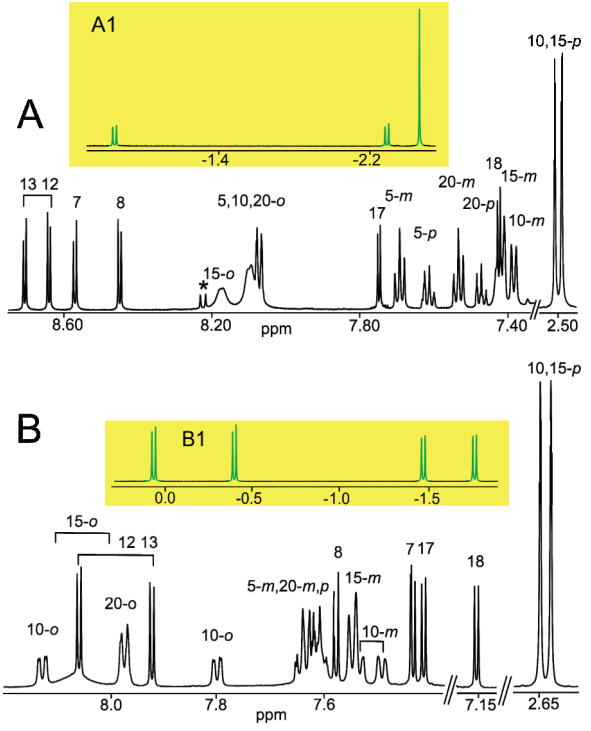
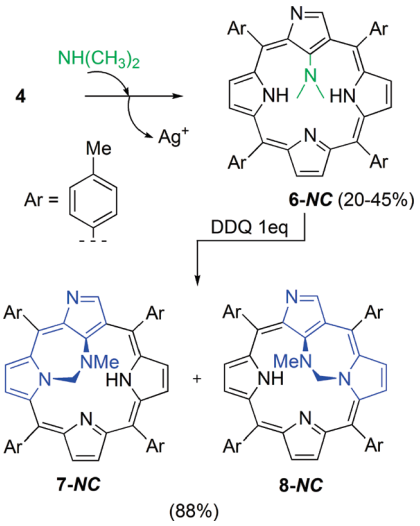


FIGURE 3. ^1H NMR spectra of **7** (A, benzene-d_6) and **9** (B, chloroform-*d*) at 298 K. Insets A1 and B1 (not to scale) show the upfield region with resonances of the inner methyl group and methylene bridge protons. Impurities observed on the spectrum of **7** are marked with *. Peak labels follow systematic position numbering of the macrocycle or denote proton groups: o, m, p (*ortho*, *meta*, and *para*) positions of *meso*-phenyl (Ph) or *meso*-*p*-tolyl rings, respectively.

SCHEME 3. Synthesis of Inner *N*-Alkylated *N*-Confused Porphyrins



methylene −1.61, −2.97 ppm) which accompanied the resembling pattern of isomeric **7**.

Significantly the regioselective amination is not limited to carbaporpholactone **1**. Thus the silver(III) complex of *N*-confused porphyrin **4** reacts with dimethylamine following similar pathways as that found for **2**. The appropriate *N*-confused analogues of **6**, **7**, and **8** (i.e., **6-*NC***, **7-*NC***, **8-*NC***) have been identified (Scheme 3). The characteristic features of monobridged species are clearly demonstrated by the X-ray crystal structure shown at Figure 4. The observed geometry is comparable to that of an inner imino substituted derivative of *N*-confused porphyrin.[17−19] The dimethylamine derivative **6-*CN*** undergoes a dynamic process already analyzed in detail for **6**, which combines an amine nitrogen inversion and a rotation around the C(21)−N bond. The line shape analysis of the dynamic N−Me_2 yielded $E_a = 28 \pm 1$ kJ/mol (6.8 ± 0.2 kcal/mol), $\Delta H^{\ddagger} = 51 \pm 2$ kJ/mol, $\Delta S^{\ddagger} = 25.0 \pm 7.5$ J/K.

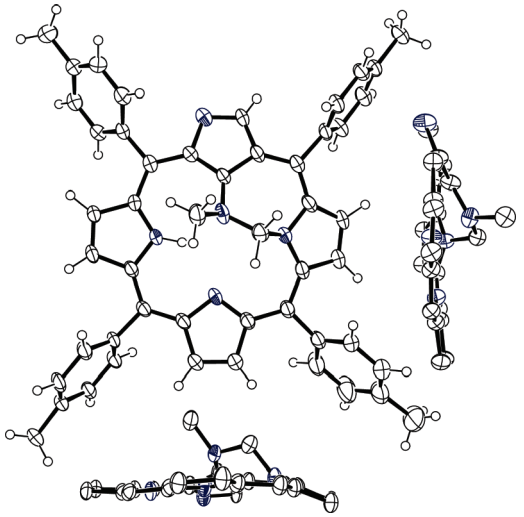


FIGURE 4. Crystal structure of **8-*NC*** (50% thermal ellipsoids; (top left) perspective view; (top right) side view; (bottom) side view; aryl groups and hydrogens omitted for clarity).

Conclusion

In the presented work we described a direct route to *N*-alkyl amination at the inner carbon of carbaporphyrinoid exemplified here mainly by carbaporpholactone **1** but extended to *N*-confused porphyrin **3**. The regioselectivity of substitution has been enforced by activation of the embedded carbocyclic fragment due to the coordination of a highly oxidized silver(III) cation. In terms of the macrocyclic chemistry, carbaporpholactone **1** and *N*-confused porphyrin **3** irreversibly trap dimethylamine which can be considered as a coordination of an organic moiety (see also other porphyrinoid examples[17,19,20]) resulting from the straightforward replacement of silver(III). In fact the incorporation of amine blocks any feasible coordination, preserving significant spectroscopic features of the free base. At the same time, the peripheral reactivity, aimed toward building for instance oligomeric structures, clearly resembles that of the original carbaporpholactone. Thus, a new route to modify the oligomeric arrays, which preserves the overall architecture but modifies an interior using the internal amination, is available.

Experimental Section

Solvents and reagents: Solvents AcOEt, MeOH, toluene, and $CHCl_3$ were used as received. CH_2Cl_2 was distilled over CaH_2. Deuterated solvents (benzene-d_6, toluene-d_8) were used as received. Chloroform-*d* was prepared directly before using by passing it through a short column with basic alumina. Dimethylamine and methylamine solutions (both 33% in ethanol) were used as received. Carbaporpholactone **1** (**1a**), *N*-confused porphyrin **3**, and their silver(III) complexes **2** and **4** were obtained according to previously described procedures.[16,21,22]

5,20-Diphenyl-10,15-ditolyl-2-oxa-3-oxo-21-*N*,*N*-dimethylaminoporphyrin (6). 2 (15 mg, 0.0195 mmol) was dissolved in 2 mL of freshly distilled dichloromethane. Then dimethylamine (30 mL of 33% solution in ethanol) was added. The mixture was stirred for 30 min and dried on a rotary evaporator. A crude green solid was dissolved in freshly distilled dichloromethane and chromatographed on a basic alumina (GII) column. The intensive green band, which eluted slowly with dichloromethane, was collected and evaporated. Yield 95%; **^{1}H NMR** (500.13 MHz, benzene-d_6, 298 K): δ = 8.38 (d, 1H, ^3J = 4.8 Hz, 13), 8.28 (d, 1H, ^3J = 4.8 Hz, 7), 8.25 (d, 1H, ^3J = 4.1 Hz, 12), 8.18−8.13 (m, 3H, 5-*o*,15-*o*), 8.02 (d, 1H, ^3J = 4.8 Hz, 8), 7.99 (d, 1H, ^3J = 4.8 Hz, 17), 7.97 (d, 2H, ^3J = 7.4 Hz, 10-*o*), 7.92 (d, 2H, ^3J = 6.86 Hz, 20-*o*), 7.87 (d, 1H, ^3J = 4.8 Hz, 18), 7.84 (dd, 1H, ^3J = 7.62 Hz, ^4J = 1.32 Hz, 15-*o*), 7.66 (t, 2H, ^3J = 7.5 Hz, 5-*m*), 7.55 (t, 1H, ^3J = 7.5 Hz, 5-*p*), 7.48 (t, 2H, ^3J = 7.5 Hz, 20-*m*), 7.39 (t, 1H, ^3J = 7.5 Hz, 20-*p*), 7.37−7.30 (m, 1H, 15-*m*), (signals of protons from 10-*m* and 15-*m* positions are partially covered by the solvent), 2.46 (s, 3H, 10-*p*), 2.43 (s, 3H, 15-*p*), −0.18 (s, 6H, N−$(CH_3)_2$) ppm; **^{13}C NMR** (125.76 MHz, benzene-d_6, 298 K): δ = 162.1 (11), 156.3, 154.89 (α), 150.5, 143.1 (14), 142.1, 140.0, 139.2, 139.0 (α), 138.0, 137.4,

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136.6 (α), 135.9 (13), 135.0 (α), 134.8 (10-*o*), 134.6 (5-*o*), 134.2 (15-*o*), 133.6, 133.5, 133.1 (12), 128.9 (20-*p*), 128.8 (8), 127.7 (5-*o*), 125.2, 122.5 (17), 122.0 (18), 121.8, 119.0, 113.3, 107.4, 40.0 (N−$(CH_3)_2$), 21.7 (10,15-*p*). Some signals are covered by the solvent; **UV−vis** (dichloromethane, λ_{max} [nm], log ε): 339 (4.42), 450 (4.86), 622 (4.09), 719 (3.86); **HRMS**, *m*/*z*: observed 703.2993 (expected 703.3067 calculated for ($C_{48}H_{38}N_4O_2 + H^+$)).

5,20-Diphenyl-10,15-ditolyl-2-oxa-3-oxo-21-*N*-methylaminoporphyrin (5). 2 (8 mg, 0.0104 mmol) was dissolved in freshly distilled toluene (2 mL). Subsequently 30 mL of methylamine (33% solution in ethanol) were added. The resulting mixture was stirred for 10 min and then dried on a rotary evaporator. A crude green solid was dissolved in toluene and chromatographed on a basic alumina (GIII) column. The intensive green band, which eluted slowly with toluene/dichloromethane v/v (1/1), was collected and evaporated to give **5**. Yield 60%. **^{1}H NMR** (500.13 MHz, benzene-d_6, 298 K): δ = 8.65 (d, 1H, ^3J = 4.1 Hz, 13), 8.55−8.52 (m, 2H, 7, 12), 8.3 (d, 1H, ^3J = 6.9 Hz, 15-*o*), 8.27−8.23 (m, 3H,5-*o*, 8), 8.22 (d, 1H, ^3J = 4.1 Hz, 18), 8.2 (d, 1H, ^3J = 4.1 Hz, 17), 8.15 (d, 2H, ^3J = 7.5 Hz, 20-*o*), 8.1−7.8 (m, 2H, 10-*o*), 7.92 (d, 1H, ^3J = 6.9 Hz, 15-*o*), 7.71 (t, 2H, ^3J = 7.5 Hz, 5-*m*), 7.64−7.54 (m, 3H, 5-*p*, 20-*m*), 7.45−7.34 (m, 20-*p*, 10-*m*, 15-*m*, this group of signal is partially covered by solvent signal), 2.49 (s, 3H, 10-*p*), 2.47 (s, 3H, 15-*p*), −1.42 (s, 3H, N−CH_3) ppm; **^{13}C NMR** (150.90 MHz, benzene-d_6, 300 K): δ = 181.0, 161.6, 152.4, 141.8, 141.1, 140.1, 139.4, 138.6, 138.1, 138.0, 137.7, 137.6, 136.9, 135.6, 135.5, 135.3 (20-*o*), 135.1 (5-*o*), 134.8 (10, 15-*o*), 134.6 (13), 134.0, 132.6 (12), 129.1, 128.9 (7), 128.8 (20-*m*), 128.7, 128.0, 127.7 (8), 124.8, 123.7 (17 or 18), 123.6 (17 or 18), 120.7, 115.0, 114.3, 109.4, 28.4 (N−(CH3)), 21.7 (10, 15-*p*). Some signals are hidden under the solvent signal; **UV−vis** (benzene, λ_{max} [nm], log ε): 334 (4.24), 445 (4.75), 601 (3.90), 693 (3.49). **HRMS**, *m*/*z*: observed 689.2883 (expected 689.2911 calculated for ($C_{47}H_{36}N_4O_2 + H^+$)).

5,20-Diphenyl-10,15-ditolyl-2-oxa-3-oxo-21−24(methylaminomethylen)fused-21-carbaporphyrin (7). 6 (5 mg, 0.00712 mmol) dissolved in 20 mL of freshly distilled dichloromethane was oxidized by addition of DDQ (1.6 mg, 1 equiv). A mixture was stirred for 10 min and dried with a rotary evaporator. The crude brown solid was dissolved in freshly distilled dichloromethane and chromatographed on a basic alumina G(II) column. The green band that eluted with dichloromethane was collected and evaporated. The subsequent column chromatography on a basic alumina G(II) column with toluene allowed the separation of **7** from traces of **8**. The first olive green fraction contains **8**, and the slower moving green one contains **7**. Yield 85% for **7**. **^{1}H NMR** (500.13 MHz, benzene-d_6, 298 K): δ = 8.7 (d, 1H, ^3J = 4.6 Hz, 12 or 13), 8.63 (d, 1H, ^3J = 4.6 Hz, 12 or 13), 8.56 (d, 1H, ^3J = 5.0 Hz, 7), 8.44 (d, 1H, ^3J = 5.0 Hz, 8), 8.2−8.12 (m, 2H, 15-*o*), 8.12−8.02 (m, 6H, 10-*o*, 5-*o*, 20-*o*), 7.74 (d, 1H, ^3J = 4.4 Hz, 17), 7.69 (t, 2H, ^3J = 7.7 Hz, 5-*m*), 7.61 (t, 1H, ^3J = 7.6 Hz, 5-*p*), 7.53 (t, 2H, ^3J = 7.4 Hz, 20-*m*), 7.47 (t, 1H ^3J = 7.4 Hz, 20-*p*), 7.44−7.41 (m, 3H, 18, 15-*m*), 7.38 (d, 2H, ^3J = 7.9 Hz, 10-*m*), 2.51 (s, 3H, 15-*p*), 2.49 (s, 3H, 10-*p*), −0.83 (d, 1H, ^2J = 11.5 Hz, N−CH*H*−N(24)), −2.28 (d, 1H, ^2J = 11.5 Hz, N−CH*H*−N-(24)), −2.45 (s, 3H, N−CH_3); **^{13}C NMR** (125.76 MHz, benzene-d_6, 298 K): δ = 164.7, 160.5 (α), 154.3 (α), 147.2 (α), 144.3 (α), 142.3, 141.9 (α), 141.8, 139.5, 138.4 (α), 138.3, 137.6 (21), 137.5, 137.0, 136.5 (15-*o*), 136.0 (12 or 13), 134.2 (5 or 10-*o*), 133.4 (20-*o*), 133.0 (12 or 13), 129.9 (7), 128.9, 128.8, 127.9, 126.3 (8), 125.3, 123.4 (17), 121.2, 120.0, 117.5, 115.0 (18), 110.2, 57.1 (N−CH*H*−N(24), N−CH*H*−N(24)), 33.8 (N−CH_3), 21.7 (10, 15-*p*). Some signals are hidden under the solvent. **UV−vis** (dichloromethane, λ_{max} [nm], log ε): 341 (4.05), 452 (4.85), 597 (3.90), 709 (3.51); **HRMS**, *m*/*z*: observed 701.2822 (expected 701.2911 calculated for ($C_{48}H_{36}N_4O_2 + H^+$)).

5,20-Diphenyl-10,15-ditolyl-2-oxa-3-oxo-22,21,24-(2-aza-1,2,3-propanetriyl)-21-carbaporphyrin (9). A 5 mg amount (0.00712 mmol) of **6** or (0.00714 mmol) of **7** was dissolved in 20 mL of freshly distilled dichloromethane, and 16 mg of DDQ (10 equiv) were added. The mixture was stirred for an additional 10 min and dried with a rotary evaporator. In each case the crude brown solid was dissolved in freshly distilled dichloromethane and chromatographed on a basic alumina column (G(III)). The green band that eluted with ethyl acetate was collected and evaporated to give **9**. Yields 77% from **6**, 57% from **7**. **^{1}H NMR** (600.13 MHz, chloroform-*d*, 300 K): δ = 8.13 (d, 1H, ^3J = 7.6 Hz, 10-*o*), 8.08−7.99 (m, 3H, 15-*o*,12 or 13), 7.97 (d, 2H, ^3J = 7.7 Hz, 20-*o*), 7.92 (d, 1H, ^3J = 4.5 Hz, 12 or 13), 7.78 (d, 1H, ^3J = 7.7 Hz, 10-*o*), 7.66−7.58 (m, 5H, 20-*m*,*p* 5-*m*), 7.57 (d, 1H, ^3J = 5.0 Hz, 8), 7.56−7.51 (m, 3H, 15-*m* 10-*m*), 7.49 (d, 1H, ^3J = 7.7 Hz, 10-*m*), 7.43 (d, 1H, ^3J = 5.1 Hz, 7), 7.41 (d, 1H, ^3J = 4.5 Hz, 17), 7.15 (d, 1H, ^3J = 4.5 Hz, 18), 2.65 (s, 3H, 15-*p*), 2.63 (s, 3H, 10-*p*), 0.06 (d, 1H, ^2J = 12.3 Hz, inner methylene), −0.40 (d, 1H, ^2J = 12.2 Hz, inner methylene), −1.48 (d, 1H, ^2J = 12.3 Hz, inner methylene), −1.77 (d, 1H, ^2J = 12.3 Hz, inner methylene). **^{13}C NMR** (150.90 MHz, chloroform-*d*, 298 K): δ = 167.0, 158.9, 153.3, 146.5, 145.1, 143.4, 141.5, 139.9, 139.6, 139.5, 138.6, 138.4, 137.5, 136.9 (10-*o*), 136.1, 135.1, 134.7 (10-*o*), 133.6 (12 or 13), 132.8, (20-*o*), 131.7 (12 or 13), 128.5 (10-*m*), 128.3 (10-*m*), 128.2 (15-*m*), 128.8 (20-*m*), 127.9 (20-*p*), 127.8, (5-*m*), 125.9 (8), 125.3, 123.1 (7), 122.5, 122.0 (17), 118.9, 116.1, 114.4 (18), 103.2, 56.8 (inner methylene), 56.5 (inner methylene), 21.6, (10 or 15-*p*), 21.5 (10 or 15-*p*). **UV−vis** (dichloromethane, λ_{max} [nm], log ε): 323 (4.24), 368 (4.22), 451 (4.52), 476 (4.43), 641 (3.79), 751 (3.64). **HRMS**, *m*/*z*: observed 699.2727 (expected 699.2754 calculated for ($C_{48}H_{34}N_4O_2 + H^+$)).

20-Phenyl-5,10,15-tritolyl-2-oxa-3-oxo-21-*N*,*N*-dimethylaminoporphyrin (6a). This derivative was synthesized according to the methodology used previously to obtain **6**. **^{1}H NMR** (600.13 MHz, benzene-d_6, 300 K): δ = 8.41−8.36 (m, 2H, 13, 7), 8.27 (d, 1H ^3J = 4.8 Hz, 12), 8.17 (dd, 1H ^3J = 7.76 Hz, ^4J = 1.63 Hz, 15-*o*), 8.12 (d, 2H, ^3J = 7.93 Hz, 5-*o*), 8.06 (d, 1H ^3J = 5.2 Hz, 8), 8.01 (d, 1H ^3J = 4.3 Hz, 17), 7.98 (d, 2H, ^3J = 6.2 Hz 10-*o*), 7.92 (d, 2H, ^3J = 7.06 Hz, 20-*o*), 7.89 (d, 1H ^3J = 4.3 Hz, 18), 7.85 (dd, 1H ^3J = 7.48 Hz, ^4J = 1.63 Hz, 15-*o*), 7.53−7.46 (m, 4H, 20-*m*, 5-*m*), 7.40 (t, 1H ^3J = 7.5 Hz, 20-*p*), 7.38−7.32 (m, 3H, 10-*m*, 15-*m*), 7.26 (15-*m* - this signal is partially covered by solvent), 2.47 (s, 3H, 5-*p*), 2.46 (s, 3H, 10-*p*), 2.43 (s, 3H, 15-*p*), −0.2 (s, 6H, N−$(CH_3)_2$) ppm. **^{13}C NMR** (150.90 MHz, benzene-d_6, 300 K) δ = 161.9 (α), 156.3, 154.8 (α), 150.6, 143.0 (α), 140.1, 139.7, 139.3, 139.2, 138.9 (α), 137.9, 137.4, 136.6 (α), 135.8 (13), 134.9 (α), 134.8 (10-*o*), 134.6 (5-*o*), 134.2 (15-*o*), 133.4, 133.1 (12), 129.6 (5-*o*), 129.1, 128.9, 128.8 (7), 127.9, 127.6 (8), 124.8, 122.5, 122.2 (17), 122.0 (18), 118.9, 113.3, 108.0, 39.9 (N−$(CH_3)_2$), 21.8 (5-*o*), 21.7 (10, 15-*o*). Some signals are hidden under solvent. **UV−vis** (dichloromethane, λ_{max} [nm], log ε): 345 (4.42), 450 (4.86), 623 (4.09), 721 (4.83). **HRMS**, *m*/*z*: observed 717.3187 (expected 717.3222 calculated for ($C_{49}H_{40}N_4O_2 + H^+$)).

20-Phenyl-5,10,15-tritolyl-2-oxa-3-oxo-21-*N*-methylaminoporphyrin (5a). This derivative was synthesized according to the methodology used previously to obtain **5**. **^{1}H NMR** (600.13 MHz, benzene-d_6, 300 K): δ = 8.65 (d, 1H ^3J = 4.7 Hz, 13), 8.64 (d, 1H, ^3J = 5.0 Hz, 7), 8.55 (d, 1H, ^3J = 4.7 Hz, 12), 8.3 (d, 1H, ^3J = 6.9 Hz, 15-*o*), 8.3 (d, 1H, ^3J = 5.0 Hz, 8), 8.25−8.18 (m, 4H, 18, 5-*o*, 17), 8.15 (d, 2H, ^3J = 7.5 Hz, 20-*o*), 8.11−7.98 (m, 2H, 10-*o*), 7.92 (d, 1H, ^3J = 6.9 Hz, 15-*o*), 7.6−7.53 (m, 4H, 5-*m*, 20-*m*), 7.49−7.29 (m, 20-*p*, 10-*m*, 15-*m*, this group of signals is partially covered by solvent signal), 2.49 (s, 6H, 5-*p*, 10-*p*), 2.47 (s, 3H, 15-*p*), −1.42 (s, 3H, 21) ppm. **^{13}C NMR** (150.90 MHz, benzene-d_6, 300 K): δ = 161.6, 157.8 (α), 152.4 (α), 141.8 (α), 140.2, 139.5, 138.6, 138.2, 138.1 (α), 137.8 (α), 137.6, 137.0 (21), 135.7 (α), 135.5, 135.3 (20-*o*), 135.2 (5-o), 134.8 (10, 15-*o*), 134.6 (13), 134.3, 132.6 (12), 132.5, 129.7 (5-*m*), 128.9, 128.8 (7), 127.9, 127.6 (8), 126.0, 124.5, 123.7 (18 and 17), 121.1, 115.1, 114.2, 109.9, 28.4 (N−CH_3), 21.8 (5-*p*), 21.7 (10, 15-*p*).

Some signals are hidden under the solvent. **UV−vis** (benzene, λ_{max} [nm], log ε): 341 (4.23), 446 (4.75), 604 (3.94), 695 (3.61). **HRMS**, *m*/*z*: observed 703.3026 (expected 703.3067 calculated for ($C_{48}H_{38}N_4O_2 + H^+$)).

20-Phenyl-5,10,15-tritolyl-2-oxa-3-oxo-21−24(methylaminomethylen)fused-21-carbaporphyrin (7a). This derivative was synthesized according to the methodology used previously to obtain **7**. **^{1}H NMR** (600.13 MHz, benzene-d_6, 300 K): δ = 8.7 (d, 1H, ^3J = 4.6 Hz, 12 or 13), 8.66 (d, 1H, ^3J = 4.9 Hz, 7), 8.63 (d, 1H, ^3J = 4.5 Hz, 12 or 13), 8.47 (d, 1H, ^3J = 4.9 Hz, 8), 0.2−8.13 (m, 2H, 15-*o*), 8.13−8.0 (m, 6H, 10-*o*, 5-*o*, 20-*o*), 7.75 (d, 1H, ^3J = 4.5 Hz, 17), 7.55−7−51 (m, 4H, 5-*m*, 20-*m*), 7.47 (t, 1H, ^3J = 7.4 Hz, 20-*p*), 7.45−7.41 (m, 3H, 18, 15-*m*), 7.38 (d, 2H, ^3J = 8.0 Hz, 10-*m*), 2.51 (s, 3H, 15-*p*), 2.50 (s, 3H, 5-*p*), 2.49 (s, 3H, 10-*p*), −0.84 (d, 1H, ^2J = 11.8 Hz, N−CH*H*−N(24)), −2.29 (d, 1H, ^2J = 11.8 Hz, N−CH*H*−N(24)),−2.44 (s, 3H, N−CH_3); **^{13}C NMR** (150.90 MHz, benzene-d_6, 300 K) δ = 164.7, 160.4 (α), 154.3 (α), 147.2 (α), 144.4 (α), 141.9 (α), 139.6, 138.5 (α), 138.3, 137.7, 137.5 (21), 137.0, 136.5 (15-*o*), 135.9 (12 or 13), 134.2 (10-*o*), 133.4 (20-*o*), 133.0 (12 or 13), 131.2, 130.0 (7), 129.4, 129.3 (5-*m*), 129.1, 128.9, 128.8, 128.0, 126.2 (8), 125.1, 123.3 (17), 121.6, 120.0, 117.4, 115.0 (18), 110.4, 57.2 (N−CH*H*−N(24), N−CH*H*−N(24)), 33.8 (N−CH_3), 21.9 (5-*p*), 21.8 (10, 15-*p*); **UV−vis** (dichloromethane, λ_{max} [nm], log ε): 346 (4.09), 453 (4.87), 599 (3.92), 710 (3.51); **HRMS**, *m*/*z*: observed 715.3033 (expected 715.3067 calculated for ($C_{48}H_{36}N_4O_2 + H^+$)).

20-Phenyl-5,10,15-tritolyl-2-oxa-3-oxo-22,21,24-(2-aza-1,2,3-propanetriyl)-21-carbaporphyrin (9a). This derivative was synthesized according to the methodology used previously to obtain **9**. **^{1}H NMR** (600.13 MHz, chloroform-*d*, 300 K): δ = 8.11 (d, 1H, ^3J = 7.6 Hz, 10-*o*), 8.08−7.99 (m, 3H, 15-*o*,12 or 13), 7.95 (d, 2H, ^3J = 7.1 Hz, 20-*o*), 7.9 (d, 1H, ^3J = 4.5 Hz, 12 or 13), 7.78 (d, 1H, ^3J = 7.6 Hz, 10-*o*), 7.65−7.56 (m, 3H, 20-*m*,*p*), 7.56−7.49 (m, 4H, 8, 15-*m* 10-*m*), 7.47 (d, 1H, ^3J = 7.7 Hz, 10-*m*), 7.44−7−35 (m, 4H, 7, 17, 5-*m*), 7.13 (d, 1H, ^3J = 4.1 Hz, 18), 2.62 (s, 3H, 15-*p*), 2.6 (s, 3H, 10-*p*), 2.54 (s, 3H, 5-*p*), 0.02 (d, 1H, ^2J = 12.1 Hz), −0.43 (d, 1H, ^2J = 12.1 Hz) −1.52 (d, 1H, ^2J = 12.2 Hz), −1.81 (d, 1H, ^2J = 12.1 Hz); **^{13}C NMR** (150.90 MHz, chloroform-*d*, 298 K): δ = 167.1, 158.9, 153.3, 147.0, 146.6, 145.3, 143.5, 141.5, 140.0, 139.7, 138.5, 137.6, 137.5, 137.0 (10-*o*), 135.6, 135.1, 134.8 (10-*o*), 133.6 (12 or 13), 132.9 (20-*o*), 131.7, 128.7 (5-*m*), 128.5 (10-*m*), 128.3 (15, 20-*m*), 128.0 (20-*p*), 125.8 (8), 125.2, 123.3, (7), 122.0 (17), 119.4, 116.1, 114.4 (18), 103.5, 56.9 (inner methylene), 56.6 (inner methylene), 22.9 (5-*p*), 21.8 (10 or 15-*p*), 21.6 (10 or 15-*p*). **UV−vis** (dichloromethane, λ_{max} [nm], log ε): 323 (4.23), 368 (4.19), 453 (4.52), 476 (4.44), 642 (3.79), 753 (3.66). **HRMS**, *m*/*z*: observed 713.2880 (expected 713.2911 calculated for ($C_{48}H_{34}N_4O_2 + H^+$)).

5,10,15,20-Tetratolyl-2-aza-21-*N*,*N*-dimethylaminoporphyrin (6-*CN*). 4 (45 mg, 0.0581 mmol) was dissolved in 2 mL of freshly distilled toluene. In the next step 30 mL of dimethylmethylamine solution (33% in ethanol) were added. The resulting mixture was refluxed for 3 h. Subsequently all solvents were removed under reduced pressure. The crude dark green solid was dissolved in freshly distilled dichloromethane and chromatographed on a basic alumina (GIII) column. The brown band (green in solution) that eluted with a dichloromethane/ethyl acetate (9/1 v/v) mixture was collected and evaporated. The extent of conversion varies from 20 to 45%. **^{1}H NMR** (500.13 MH, benzene-d_6, 298 K): δ = 8.55 (d, 1H, ^3J = 4.93 Hz, 7), 8.53 (d, 1H, ^3J = 4.82 Hz, 13), 8.51−8.48 (m, 2H, 18, 12), 8.28 (d, 1H, ^3J = 4.93 Hz, 8), 8.25 (d, 1H, ^3J = 4.6 Hz, 17), 8.15 (dd, 1H, ^3J = 7.52 ^4J = 1.15 Hz, 15-*o*), 8.11 (d, 1H, ^3J = 7.11 Hz, 10-*o*) 8.02−7.96 (m, 3H, 10-*o*, 5-*o*), 7.92 (dd, 1H, ^3J = 7.52 ^4J = 1.15 Hz, 15-*o*), 7.4 (d, 2H, ^3J = 7.85, 20-*m*), 7.41−7.36 (m, 2H, 10-*m*, 15-*m*), 7.36−7.30 (m, 3H, 5-*m*, 10-*m*), 6.6 (s, 1H, 3), 2.48 (s, 3H, 10-*p*), 2.46 (s, 3H, 15-*p*), 2.43 (s, 3H, 20-*p*), 2.41 (s, 3H, 5-*p*), −0.34 (s, 6H, N−$(CH_3)_2$), one signal is overlapping with the solvent. The signals of protons from the 20-*o* position are too broad to be observed at 298 K. **^{13}C NMR** (125.76 MHz, benzene-d_6, 298 K): δ = 160.6 (α), 157.8 (α), 143.6 (21), 143.0 (α), 140.5 (α), 140.3, 140.0, 138.9, 138.8, 138.5, 137.9 (3), 137.6, 137.5, 137.3, 136.8, 135.9 (α, 13), 134.9 (10-*o*), 134.7 (18, 15-o), 134.5 (10-*o*), 134.4 (15-*o*), 133.4, 128.9, 128.0, 127.9 (7), 126.3 (18), 125.7 (8), 123.8 (17), 122.3, 119.7, 114.8, 41.4, (N−$(CH_3)_2$) 21.7 (5, 10, 15, 20-*p*). Some signals are covered by the solvent signal. **UV−vis** (dichloromethane, λ_{max} [nm], log ε): 304 (4.34), 348 (4.36) 416 (4.99), 635 (9.97), 798 (3.63). **HRMS**, *m*/*z*: observed 714.3522 (expected 714.3591 calculated for ($C_{50}H_{43}N_5 + H^+$)).

5,10,15,20-Tetratolyl-2-aza-21−22(methylaminomethylen)-fused-21-carbaporphyrin (8-*NC*) and 5,10,15,20-Tetratolyl-2-aza-21−24(methylaminomethylen)-fused-21-carbaporphyrin (7-*NC*). 6-*NC* (15 mg, 0.0210 mM) was dissolved in 20 mL of freshly distilled dichloromethane, and DDQ (4.7 mg, 1 equiv) was added. The mixture was stirred for 10 min and then dried on a rotary evaporator. The crude brown solid was dissolved in freshly distilled dichloromethane and chromatographed on abasic alumina (GII) column. The strong green band that eluted with dichloromethane was collected and evaporated. Yield: 88%. The formation of small amounts of these compounds was also observed during a reaction between the silver(III) complex of *N*-confused porphyrin and dimethylamine. Two isomers were separated by flash column chromatography using basic alumina (GII). The first separation was not complete. The differences in shade "on column" allowed collection of fractions containing more than 90% of each isomer. The first light green fraction contained the 21−24 bridged compound **7-*NC***. The third olive green fraction contained mostly the 21−22 **8-*NC***. The middle fraction contained both isomers. The independent chromatography of the first and third fractions under identical conditions yielded **7-*NC*** and **8-*NC***. **HRMS**, *m*/*z*: observed 712.3385 (expected 712.3434 calculated for ($C_{50}H_{41}N_5 + H^+$)).

Spectroscopic data for **8-*NC***: **^{1}H NMR** (600.13 MHz, benzene-d_6, 300 K): δ = 8.68 (d, 1H, ^3J = 4.6 Hz, 18), 8.65 (d, 1H, ^3J = 4.5 Hz, 13 or 12), 8.60 (d, 1H, ^3J = 4.6 Hz, 13 or 12), 8.44 (d, 1H, ^3J = 4.6 Hz, 17), 8.21 (s, 1H, 3), 8.2−8.0 (m, 4H, 10-*o*, 15-*o*), 7.91 (d, 1H, ^3J = 4.8 Hz, 7), 7.83 (d, 1H, ^3J = 4.7 Hz, 8), 7.74 (d, 2H, ^3J = 7.9 Hz, 5-*o*), 7.48−7.39 (m, 3H, 10-*m*, 20-*m*), 7.36 (d, 2H, ^3J = 7.9 Hz, 15-*m*), 7.20 (d, 2H, ^3J = 7.9 Hz, 5-*m*), 2.52 (s, 3H, 10 or 20-*p*), 2.48 (s, 3H, 15-*p*), 2.46 (s, 3H, 10 or 20-*p*), 2.36 (s, 3H, 5-*p*), −1.15 (d, 1H, ^2J = 11.3 Hz, N−CH*H*−N(22)), −1.72 (s, 3H, N−CH_3), −2.51 (d, 1H, ^2J = 11.1 Hz, N−CH*H*−N(22)); **^{13}C NMR** (150.90 MHz, benzene-d_6, 300 K) δ = 158.7, 158.4, 150.8 (3), 150.3, 146.1, 142.1, 140.4, 140.0, 139.9, 139.7, 139.5, 137.9, 137.7, 137.5, 137.3, 136.7. 136.2, 135.4 (12 or 13), 134.8 (12 or 13), 133.8 (5-*o*), 130.2, 129.9, 129.1, 128.9 (18), 128.8, 128.0, 124.8 (8), 123.9 (17), 122.1, 121.9 (7), 119.3, 58.9 (N−CH*H*−N(22), N−CH*H*−N(22)), 37.3 (N−CH_3), 21.8 (10, 15 20-*p*), 21.6 (5-*p*). Some signals are covered by the solvent signal. **UV−vis** (CH_2Cl_2, λ_{max} [nm], log ε): 303 (4.26), 417 (4.89), 621 (3.84), 799 (5.50).

Spectroscopic data for **7-*NC***: **^{1}H NMR** (600.13 MHz, benzene-d_6, 300 K): δ = 8.59−8.57 (m, 2H, 12,7), 8.55 (d, 1H, ^3J = 4.5 Hz, 13), 8.39 (d, 1H, ^3J = 4.8 Hz, 8), 8.25 (d, 2H, ^3J = 7.9 Hz, 20-*o*), 8.22 (s, 1H, 3), 8.19−8.04 (m, 4H, 15-*o*, 10-*o*), 7.96−7.82 (bs, 2H, 5-*o*), 7.66 (d, 1H, ^3J = 4.5 Hz, 18), 7.59 (d, 1H, ^3J = 4.5 Hz, 17), 7.43−7.39 (m, 4H, 15-*m*, 20-*m*), 7.38 (d, 2H, 8.0, ^3J = Hz, 10-*m*), 7.26 (m, 5-*m*, this signal is partially covered under solvent signal), 2.5 (s, 3H, 15-*p*), 2.48 (s, 3H, 10-*p*), 2.44 (s, 3H, 20-*p*), 2.4 (s, 3H, 5-*p*), −0.53 (d, 1H, ^2J = 11 Hz, N−CH*H*−N-(24)), −1.76 (s, 3H, N−CH_3), −1.92 (d, 1H, ^2J = 11 Hz, N−CH*H*−N(24)). **^{13}C NMR** (150.90 MHz, benzene-d_6, 300

K) δ = 160.7, 156.8, 156.6 (3), 148.0, 147.4, 143.2, 142.8, 141.9, 139.7, 138.6, 137.9, 137.8, 137.4, 137.3, 137.2, 136.6 (15-*o*), 135.9 (12), 135.3 (20-*o*), 133.9, 133.8 (13), 129.7 (7), 128.8, 128.0, 125.2(8), 124.1, 124.0, 122.6 (17), 122.4, 119.2 (18), 117.4, 57.9 (N−CH***H***−N(24), N−C**H*H*−N(24)), 36.7 (N−CH_3), 21.7 (10, 15 20-*p*), 21.6 (5-*p*). Some signals are covered by the solvent. **UV−vis** (dichloromethane, λ_{max} [nm], log ε): 303 (4.29), 418 (4.90), 623 (3.95), 792 (5.58).

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Supporting Information Available: Additional spectral data (^{1}H and ^{13}C) for **5**, **6**, **7**, **9**, **6-*NC***, **7-*NC***, **8-*NC*** and X-ray details for **8-*NC***. This material is available free of charge via the Internet at http://pubs.acs.org.