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Synthesis of A_2B_2 type *cis*-doubly N-confused porphyrins from N-confused dipyrromethanes

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Abstract—A_2B_2 type of *cis*-doubly N-confused porphyrins (*cis*-N_2CP) bearing 2,6-dichloro-, 2-nitro-, 3-nitro-, and 4-nitro-phenyl groups and pentafluorophenyl groups at *meso*-positions were synthesized by the condensation of aryl-substituted N-confused dipyrromethanes and pentafluorobenzaldehyde. The complexation of rare high oxidation states of metals, Cu(III) and Ag(III), was demonstrated.

1. Introduction

In the last decade, there is a considerable progress in the synthesis and structural characterization of a variety of porphyrin analogs, including porphyrin isomers. Among such porphyrinoids,[1] N-confused porphyrin (NCP) and its higher homologs, multiply N-confused porphyrins, are of particular interest because they exhibit unusual physical property, chemical reactivity and coordination chemistry.[2–4] Lately, the second generation of NCP, *cis*-doubly N-confused porphyrin (*cis*-N_2CP), has been synthesized and the complexation of rare high oxidation state of metals, Cu(III) and Ag(III), was demonstrated by NMR and X-ray crystallography.[5,6] Remarkably, high efficient photosensitization for the singlet oxygen by the latter Ag(III) complex was recently revealed.[6] In the original synthesis of *cis*-N_2CP, an acid-catalyzed [2+2] condensation of N-confused dipyrromethane bearing pentafluorophenyl (C_6F_5) group at *meso*-position (**1**) and pentafluorobenzaldehyde was used. The electron-withdrawing groups were considered effective for the stabilization of multiply N-confused isomers because the corresponding tetraphenyl derivative could not be isolated at all in a similar procedure.[2a,7] To clarify the scope of this condensation reaction and generality of the peculiar metal coordination, we have examined the synthesis of *cis*-N_2CP derivatives bearing different electron-withdrawing aryl groups, such as 2,6-dichloro-, 2-nitro-, 3-nitro-, and 4-nitro-phenyl. *cis*-N_2CP derivatives (**6-10**) were obtained in 0.4–2.0% yields and afforded the corresponding Cu(III) and Ag(III) complexes. Details of the synthesis and the weak aromatic nature of the *cis*-N_2CP derivatives are reported. (Chart 1).

2. Results and discussion

The synthesis was performed by the [2+2] condensation of aryl substituted α,β′-dipyrromethane (N-confused dipyrromethane) and arylaldehyde.[5a] In order to prevent the fragmentation and scrambling of the intermediates during the acid-catalyzed reaction, electron-withdrawing substituents, pentafluorobenzaldehyde, 2,6-dichlorophenyl, 2-,

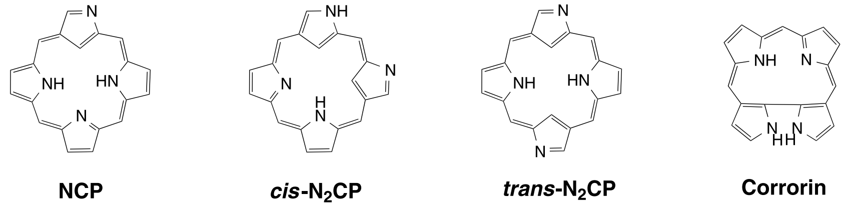

Chart 1. Framework of N-confused porphyrins: NCP, *cis*-N_2CP, *trans*-N_2CP, and Corrorin.

Keywords: Porphyrin; N-Confused porphyrin; N-Confused dipyrromethane; Cu(III); Ag(III).

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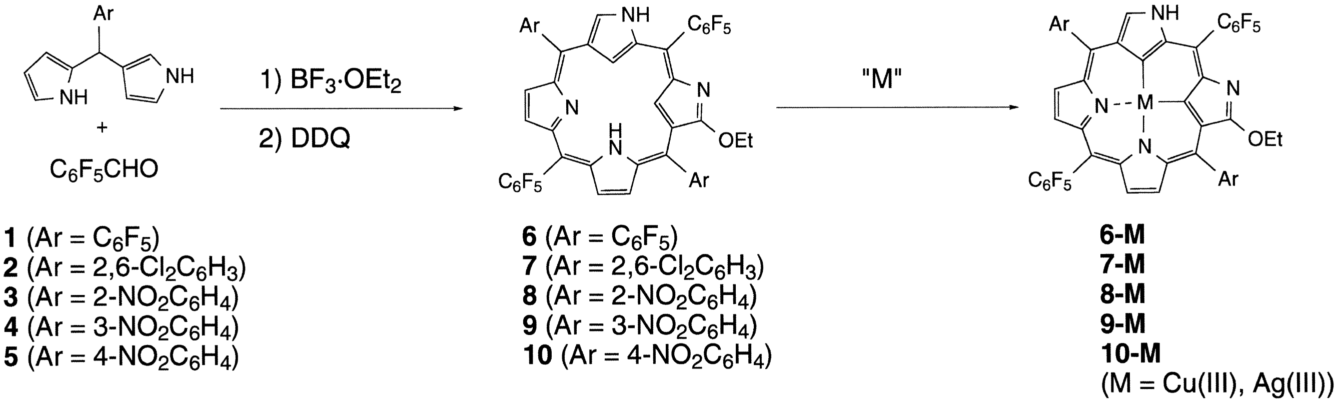
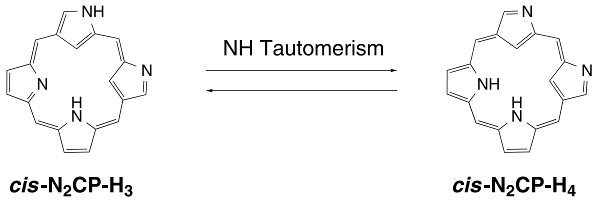


Scheme 1. Synthesis of (a) *cis*-N_2CP (**6-10**) and (b) Cu(III) and Ag(III) complexes (**6-10-M**).

3-, and 4-nitrophenyl N-confused dipyrromethanes (**1-5**) were used.[8] At first, the dipyrromethanes (**1-5**) were reacted with pentafluorobenzaldehyde in the presence of $BF_3 \cdot OEt_2$ in $CHCl_3$ containing 0.5% ethanol. After stirring for 2 h, the reaction mixture was passed through a short silica gel column to remove the polymerized products. The eluted solution was then oxidized by 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) for 1 h at room temperature. After the repeated column chromatography, the *cis*-N_2CP (**6-10**) were obtained in 2.0, 0.4, 0.8, 1.8, and 0.6%, respectively. (Scheme 1) In each case, an ethoxy group, which was derived from the solvent, was substituted at the α-position of one of the confused pyrroles. Apart from *cis*-N_2CP, a new type of corrole isomer, corrorin, was also obtained as a side-product in the reaction with dipyrromethanes, **1** and **3**, in the respective yields of 13 and 0.7%.[5c] Under these synthetic conditions, *trans*-type of N_2CP (*trans*-N_2CP),[9] in which two confused pyrroles are located in the opposite sides in the core, was not isolated, probably due to the higher reactivity of the α-position of normal pyrrole than that of confused pyrrole in the N-confused dipyrromethanes **1-5**.[10]

When N-confused dipyrromethane bearing a phenyl group was used in place of **1-5**, the scrambling products, NCP having two or three C_6F_5-substituents, were obtained as judged by the ^1H NMR, UV/vis absorption spectra, and FABMS. Furthermore, the condensation of *meso*-free N-confused dipyrromethane and pentaflurobenzaldehyde did not afford the confused analogs but several kinds of porphyrins, as a result of the fragmentation of starting materials. These results infer that the electron-withdrawing group is essential for the formation of *cis*-N_2CP. On the other hand, the condensation between pentafluorophenyl-substituted dipyrromethane (**1**) and 2,6-dichlorobenzaldehyde afforded only a trace of *cis*-N_2CP (**11**). Thus, pentafluorobenzaldehyde also plays a key role in the synthesis of a series of *cis*-N_2CP.[11]

In each *cis*-N_2CP (**6-10**), the macrocycle possesses three hydrogens in the core (***cis*-N_2CP-H_3**). Another possible NH tautomeric form, ***cis*-N_2CP-H_4**, was not observed in $CDCl_3$ solution, which was well consistent with the results of the DFT calculations.[7d] (Scheme 2) As seen in the ^1H NMR spectra, the peripheral protons were observed in the weak aromatic region, 6.69–7.46 ppm along with the outer NH around 8.93–9.00 ppm (Table 1). Furthermore, a pair of inner CH signals were observed at 3.12–3.38 and 3.42–3.73 ppm, respectively, and the signals at 6.15–6.50 ppm were assignable to the inner NH, suggesting the less aromatic feature of *cis*-N_2CP. Disruption of the full conjugated π-circuit at the confused pyrrole rings seems to be compensated by the stabilization of the intramolecular hydrogen bonding in the core.[7d]



Scheme 2. NH-tautomers of *cis*-N_2CP.

Table 1. Selective ^1H NMR chemical shifts (ppm, $CDCl_3$) of N_2CP (**6-10**)

	6	7	8[a]	9	10
Outer NH	8.95	9.00	8.97	8.93	8.97
βH	7.36	7.29	7.28	7.38	7.46
βH	7.28	7.20	7.12/7.07	7.26	7.35
βH	7.06	7.06	6.92–6.88	6.97	7.03
βH	6.98	6.98	6.92–6.88	6.94	7.00
αH	6.94	6.97	6.69	6.71	6.79
Inner NH	6.38	6.30	6.50	6.15	6.24
Inner CH	3.50	3.42	3.73/3.70	3.45	3.57
Inner CH	3.20	3.12	3.38	3.20	3.28

[a] Due to the existence of two atropisomers, the signals are overlapped.

Table 2. UV/vis absorption bands (λ_{max}, nm) of **6-10** in $CHCl_3$

	Absorption bands
6	347.0, 424.0, 627.5, 667.5
7	345.5, 438.5, 621.0
8	345.5, 428.5, 642.5, 674.0
9	345.0, 435.0, 633.0, 676.5
10	346.5, 435.0, 690.0
6-Cu	368.0, 441.0, 612.5
7-Cu	370.0, 444.0, 619.0
8-Cu	368.5, 445.0, 624.0
9-Cu	368.0, 444.5, 619.0
10-Cu	368.0, 447.5, 621.0
6-Ag	368.0, 442.5, 620.0, 676.0
7-Ag	368.0, 443.5, 626.5, 670.5
8-Ag	367.0, 444.5, 517.5, 630.0, 672.0
9-Ag	365.5, 445.0, 515.0, 584.5, 627.5, 671.5
10-Ag	367.5, 448.5, 629.5, 671.5

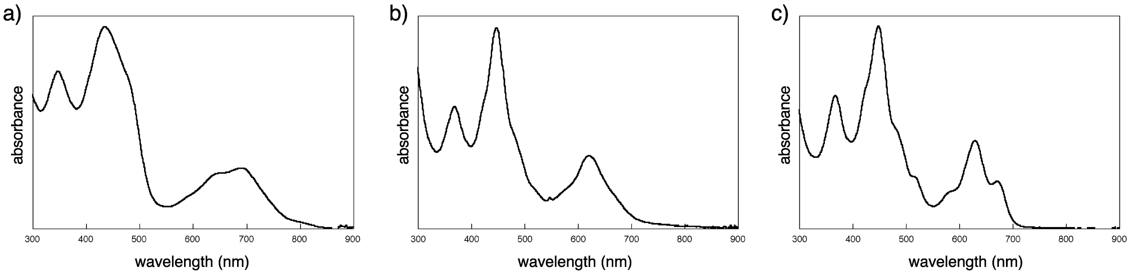


Figure 1. UV/vis absorption spectra of (a) **10**; (b) **10-Cu**, and (c) **10-Ag** in $CHCl_3$.

Next, the coordination chemistry of *cis*-N_2CP (**6-10**) was examined. Like *cis*-N_2CP bearing pentafluorophenyl groups (**6**),[5a] the doubly N-confused isomers (**7-10**) also coordinated with copper and silver ions to afford the complexes (**7-10-M**) with rare high oxidation states, Cu(III) and Ag(III). (Scheme 1) In each complex, **6-10-M**, the ^1H NMR signals were observed in a normal diamagnetic region, 7.73–8.31 and 7.66–8.28 ppm, for the peripheral protons, and 10.02–10.35 and 9.93–10.37 ppm for outer NH, in Cu(III) and Ag(III) complexes, respectively, suggesting the trianionic behavior of the ligand macrocycles and the coordination of +3 cation center. The lower field shifts of these metal complexes compared to the free bases (**6-10**) is reflected from the more planar structures elucidated in **6-Cu** and **6-Ag** in the solid states.[5a]

The absorption maxima of *cis*-N_2CP and the Cu(III) and Ag(III) complexes in $CHCl_3$ are summarized in Table 2. As representatives, the absorption spectra of **10** and the metal complexes (**10-M**) are shown in Figure 1. In the free base, Cu(III) and Ag(III) complexes of **7-10**, the wavelengths of the Soret-like and Q-bands are bathochromically shifted compared with those of **6** and its metal complexes. For example, the Soret-like bands of **10-M** (M=H_3, Cu, Ag) appear at 435.0, 447.5, and 448.5 nm, which are 9.0, 6.5, and 6.0 nm shifted to the longer wavelength compared with **6-M** (M=H_3, Cu, Ag). Similar tendencies are observed also in Q-bands.[12] In the present cases, even two different substituents of A_2B_2 system affect the electronic states largely. Thus, if the synthetic methods for various *cis*-N_2CP derivatives are established, a fine tuning of the absorption bands would make these porphyrin analogs more attractive for the application such as photodynamic therapy (PDT) which requires the photosensitizer to absorb at the red region of the visible spectrum (>650 nm) suitable for the penetration of light through the skin into the tissue.[13,14]

3. Summary and conclusions

In summary, *cis*-N_2CP (**7-10**) bearing 2,6-dichloro-, 2-nitro-, 3-nitro-, and 4-nitro-phenyl *meso*-substituents are synthesized from the respective N-confused dipyrromethanes (**2-5**) and pentafluorobenzaldehyde. These *cis*-N_2CP derivatives stabilize the rare higher oxidation state, Cu(III) and Ag(III), in the core similarly to the tetrakis(pentafluorophenyl)-substituted *cis*-N_2CP (**6**). Under the same reaction conditions, N-confused dipyrromethane bearing a phenyl group does not afford the *cis*-N_2CP but scrambled into NCP. Modification of the *meso*-substituents of *cis*-N_2CP may be useful for the development of functional materials such as PDT sensitizers.

4. Experimental

4.1. General

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 a Shimadzu UV-3100PC spectrometer. ^1H NMR spectra were recorded on a JEOL α-500 spectrometer (operating as 500.00 MHz for ^1H) using the residual solvent as the internal reference. Fast atom bombardment mass spectrometry (FABMS) was recorded on a JEOL-HX110 in the positive ion mode with a 3-nitrobenzylalcohol matrix. N-confused dipyrromethanes (**2-5**) were prepared according to the literature.[8]

4.1.1. N-Confused 5-(2′,6′-dichlorophenyl)dipyrromethane (2). In 26% yield. ^1H NMR ($CDCl_3$, 500 MHz, 27 °C): δ (ppm) 8.27 (s, br, 1H, NH), 8.13 (s, br, 1H, NH), 7.30 (d, *J*=8.5 Hz, 2H, *m*-Ar), 7.10 (t, *J*=8.5 Hz, 1H, *p*-Ar), 6.78 (dd, *J*=5.0, 2.0 Hz, 1H, αH), 6.68 (s, 2H, αH), 6.38 (s, 1H, βH), 6.25 (d, *J*=1.5 Hz, 1H, βH), 6.18 (dd, *J*=5.5, 2.5 Hz, 1H, βH), 5.97 (s, 1H, *meso*H). FABMS: *m/z* (% intensity) 290.1 (100, M^+). Calcd for $C_{15}H_{12}Cl_2N_2$, 290.04.

4.1.2. N-Confused 5-(2′-nitrophenyl)dipyrromethane (3). In 40% yield. ^1H NMR ($CDCl_3$, 500 MHz, 27 °C): δ (ppm) 8.10 (s, br, 2H, NH), 7.79 (d, *J*=8.0 Hz, 1H, *m*-Ar), 7.48 (m, 1H, *p*-Ar), 7.37 (d, *J*=8.0 Hz, 1H, *o*-Ar), 7.33 (m, 1H, *m*-Ar), 6.75 (m, 1H, αH), 6.70 (m, 1H, αH), 6.51 (s, 1H, αH), 6.15 (m, 1H, βH), 6.10 (s, 1H, βH), 6.06 (s, 1H, βH), 5.89 (s, 1H, *meso*-H). FABMS: *m/z* (% intensity)=267.2 (100, M^+). Calcd for $C_{15}H_{13}N_3O_2$, 267.10.

4.1.3. N-Confused 5-(3′-nitrophenyl)dipyrromethane (4). In 12% yield. ^1H NMR ($CDCl_3$, 500 MHz, 27 °C): δ (ppm) 8.15 (s, br, 1H, NH), 8.13 (t, *J*=2.0 Hz, 1H, *o*-Ar), 8.07 (m, 1H, *p*-Ar), 7.99 (s, br, 1H, NH), 7.59 (d, *J*=8.0 Hz, 1H, *o*-Ar), 7.45 (t, *J*=8.0 Hz, 1H, *m*-Ar), 6.79 (dd, *J*=4.5, 2.5 Hz, 1H, αH), 6.71 (dd, *J*=4.0, 2.5 Hz, 1H, αH), 6.51 (d, *J*=2.0 Hz, 1H, αH), 6.16 (dd, *J*=4.0, 2.5 Hz, 1H, βH), 6.08 (dd, *J*=4.5, 2.5 Hz, 1H, βH), 5.83 (s, 1H, βH), 5.48 (s, 1H, *meso*-H). FABMS: *m/z* (% intensity)=267.1 (100, M^+). Calcd for $C_{15}H_{13}N_3O_2$, 267.10.

4.1.4. N-Confused 5-(4′-nitrophenyl)dipyrromethane (5). In 11% yield. ^{1}H NMR (CDCl$_3$, 500 MHz, 27 °C): δ (ppm) 8.15 (s, br, 1H, NH), 8.14 (d, J=8.5 Hz, 2H, *m*-Ar), 7.99 (s, br, 1H, NH), 7.40 (d, J=8.5 Hz, 2H, *m*-Ar), 6.79 (dd, J=5.0, 2.5 Hz, 1H, αH), 6.71 (dd, J=4.0, 2.5 Hz, 1H, αH), 6.49 (d, J=2.0 Hz, 1H, αH), 6.17 (dd, J=4.0, 3.0 Hz, 1H, βH), 6.07 (dd, J=4.0, 2.5 Hz, 1H, βH), 5.85 (s, 1H, βH), 5.48 (s, 1H, *meso*-H). FABMS: *m*/*z* (% intensity)=267.2 (100, M$^+$). Calcd for $C_{15}H_{13}N_3O_2$, 267.10.

4.2. General procedures for *cis*-doubly N-confused porphyrins (*cis*-N$_2$CP)[5a]

To a solution of N-confused dipyrromethane (**2**-**5**) (1.5 mmol), pentafluorobenzaldehyde (294 mg, 1.5 mmol), and Bu$_4$NBr (242 mg, 0.75 mmol) in 0.5% EtOH–CHCl$_3$ (750 ml), BF$_3$OEt$_2$ (189 μl, 1.5 mmol) were added and the solution was stirred for 2 h at room temperature. The reaction mixture was then passed through a silica gel column (Wakogel C-200) and eluted with CHCl$_3$. To a combined solution, DDQ (510 mg, 2.25 mmol) was added and stirred for 1 h at room temperature. The green colored product was separated by silica gel column chromatography (2% MeOH/CH$_2$Cl$_2$, Wakogel C-200 and C-300) and size-exclusion chromatography, followed by recrystallization from hexane/CH$_2$Cl$_2$ to give N$_2$CP as a green solid.

4.2.1. 2-Ethoxy-10,20-bis(2′,6′-dichlorophenyl)-5,15-bis-(pentafluorophenyl)-3,7-diaza-21,22-dicarbaporphyrin (7). In 0.4% yield. R_f=0.40 (CH$_2$Cl$_2$). ^{1}H NMR (CDCl$_3$, 500 MHz, 27 °C): δ (ppm) 9.00 (br, 1H, outer NH), 7.60–7.40 (m, 6H, Ar), 7.29 (d, J=5.0 Hz, 1H, βH), 7.20 (d, J=5.0 Hz, 1H, βH), 7.06 (d, J=5.0 Hz, 1H, βH), 6.98 (d, J=5.0 Hz, 1H, βH), 6.97 (s, 1H, αH), 6.30 (br, 1H, inner NH), 4.24 (q, J=7.0 Hz, 2H, CH$_2$O), 3.42 (s, 1H, inner CH), 3.12 (s, 1H, inner CH), 1.00 (t, J=7.0 Hz, 3H, CH$_3$). UV/vis (CHCl$_3$): λ_{max} (nm) 345.5, 438.5, 621.0. FABMS: *m*/*z* (% intensity)=973.9 (75, M$^+$), 976.0 (100, M$^+$+2). Calcd for $C_{46}H_{20}Cl_4F_{10}N_4O$, 974.02.

4.2.2. 2-Ethoxy-10,20-bis(2′-nitrophenyl)-5,15-bis(pentafluorophenyl)-3,7-diaza-21,22-dicarbaporphyrin (8). In 0.8% yield. Due to the sterically hindered *ortho*-nitro group, two kinds of diastereomeric atropisomers of **8** could exist in the ratio of ca. 3:2 according to the configuration of two *o*-nitro substituents; *anti* and *syn* toward the porphyrin plane. In the ^{1}H NMR spectrum in CDCl$_3$ at 55 °C, the coalescence of the peaks was not observed due to the existence of two isomers. R_f=0.16 (CH$_2$Cl$_2$). ^{1}H NMR (CDCl$_3$, 500 MHz, 27 °C): δ (ppm) 8.97 (br, 1H, outer NH), 8.24–8.17 (m, 2H, *m*-Ar), 7.81–7.69 (m, 6H, Ar), 7.28 (d, J=5.0 Hz, 1H, βH), 7.12 or 7.07 (d, J=5.5 Hz, 1H, βH), 6.92–6.88 (m, 1H, βH), 6.69 (s, 1H, αH), 6.50 (br, 1H, inner NH), 4.21/4.15 (m, 2H, CH$_2$O), 3.73 or 3.70 (s, 1H, inner CH), 3.38 (s, 1H, inner CH), 0.89 (t, J=7.0 Hz, 3H, CH$_3$). UV/vis (CHCl$_3$): λ_{max} (nm) 345.5, 428.5, 642.5, 674.0. FABMS: *m*/*z* (% intensity)=928.1 (65, M$^+$), 929.1 (100, M$^+$+1). Calcd for $C_{46}H_{22}F_{10}N_6O_5$, 928.15.

4.2.3. 2-Ethoxy-10,20-bis(3′-nitrophenyl)-5,15-bis(pentafluorophenyl)-3,7-diaza-21,22-dicarbaporphyrin (9). In 1.8% yield. R_f=0.30 (CH$_2$Cl$_2$). ^{1}H NMR (CDCl$_3$, 500 MHz, 27 °C): δ (ppm) 8.93 (br, 1H, outer NH), 8.56 (t, J=2.0 Hz, 1H, *o*-Ar), 8.41 (t, J=2.0 Hz, 1H, *o*-Ar), 8.38 (m, 1H, *p*-Ar), 8.29 (m, 1H, *p*-Ar), 7.69 (t, J=8.0 Hz, 1H, *m*-Ar), 7.60 (t, J=8.0 Hz, 1H, *m*-Ar), 7.38 (d, J=5.0 Hz, 1H, βH), 7.26 (d, J=5.5 Hz, 1H, βH), 6.97 (d, J=5.0 Hz, 1H, βH), 6.94 (d, J=5.5 Hz, 1H, βH), 6.71 (dd, 1H, αH), 6.15 (br, 1H, inner NH), 4.11 (q, J=7.0 Hz, 2H, CH$_2$O), 3.45 (s, 1H, inner CH), 3.20 (s, 1H, inner CH), 0.82 (t, J=7.0 Hz, 3H, CH$_3$). UV/vis (CHCl$_3$): λ_{max} (nm) 345.0, 435.0, 633.0, 676.5. FABMS: *m*/*z* (% intensity)=928.0 (50, M$^+$), 929.0 (100, M$^+$+1). Calcd for $C_{46}H_{22}F_{10}N_6O_5$, 928.15.

4.2.4. 2-Ethoxy-10,20-bis(4′-nitrophenyl)-5,15-bis(pentafluorophenyl)-3,7-diaza-21,22-dicarbaporphyrin (10). In 0.6% yield. R_f=0.36 (CH$_2$Cl$_2$). ^{1}H NMR (CDCl$_3$, 500 MHz, 27 °C): δ (ppm) 8.97 (br, 1H, outer NH), 8.43 (d, J=9.0 Hz, 2H, *m*-Ar), 8.36 (d, J=9.0 Hz, 2H, *m*-Ar), 7.93 (d, J=9.0 Hz, 2H, *o*-Ar), 7.78 (d, J=9.0 Hz, 2H, *o*-Ar), 7.46 (d, J=5.0 Hz, 1H, βH), 7.35 (d, J=5.0 Hz, 1H, βH), 7.03 (d, J=5.0 Hz, 1H, βH), 7.00 (d, J=5.0 Hz, 1H, βH), 6.79 (s, 1H, αH), 6.24 (br, 1H, inner NH), 4.19 (q, J=7.0 Hz, 2H, CH$_2$O), 3.57 (s, 1H, inner CH), 3.28 (s, 1H, inner CH), 0.91 (t, J=7.0 Hz, 3H, CH$_3$). UV/vis (CHCl$_3$): λ_{max} (nm) 346.5, 435.0, 690.0. FABMS: *m*/*z* (% intensity)=928.2 (80, M$^+$), 929.2 (100, M$^+$+1). Calcd for $C_{46}H_{22}F_{10}N_6O_5$, 928.15.

4.2.5. 21-Chloro-2-ethoxy-10,20-bis(4′-nitrophenyl)-5,15-bis(pentafluorophenyl)-3,7-diaza-21,22-dicarbaporphyrin (10-Cl). In 0.3% yield as a byproduct of **10**. R_f=0.35 (CH$_2$Cl$_2$). ^{1}H NMR (CDCl$_3$, 500 MHz, 27 °C): δ (ppm) 8.98 (br, 1H, outer NH), 8.41 (d, J=9.0 Hz, 2H, *m*-Ar), 8.36 (d, J=9.0 Hz, 2H, *m*-Ar), 7.90 (d, J=9.0 Hz, 2H, *o*-Ar), 7.81 (d, J=9.0 Hz, 2H, *o*-Ar), 7.46 (d, J=5.0 Hz, 1H, βH), 7.35 (d, J=5.0 Hz, 1H, βH), 7.01 (d, J=5.0 Hz, 1H, βH), 6.92 (d, J=5.0 Hz, 1H, βH), 6.78 (s, 1H, αH), 6.26 (br, 1H, inner NH), 4.12 (m, 1H, CH$_2$O), 3.93 (m, 1H, CH$_2$O or CH$_3$), 3.62 (s, 1H, inner CH), 0.83 (t, J=7.0 Hz, 3H, CH$_3$). UV/vis (CHCl$_3$): λ_{max} (nm) 358.5, 443.0, 667.0. FABMS: *m*/*z* (% intensity)=962.1 (90, M$^+$), 963.1 (100, M$^+$+1). Calcd for $C_{46}H_{21}ClF_{10}N_6O_5$, 962.11.

4.3. General procedures for Cu(III) complexes of *cis*-doubly N-confused porphyrins (*cis*-N$_2$CP-Cu)

To a solution of ethoxy substituted tetraaryl-N$_2$CP (**7**-**10**) (0.020 mmol) in 20 ml of CHCl$_3$, Cu(OAc)$_2$ (2.6 mg, 0.021 mmol) was added and the solution was stirred at room temperature overnight. The solution was filtered through a silica gel column (Wakogel C-200) to remove the excess copper salt and the filtrate was evaporated. Recrystallization from hexane/CH$_2$Cl$_2$ gave N$_2$CP-Cu as a green solid.

4.3.1. Cu(III) Complex of 2-ethoxy-10,20-bis(2′,6′-dichlorophenyl)-5,15-bis(pentafluorophenyl)-3,7-diaza-21,22-dicarbaporphyrin (7-Cu). In a quantitative yield. R_f=0.40 (CH$_2$Cl$_2$). ^{1}H NMR (CDCl$_3$, 500 MHz, 27 °C): δ (ppm) 10.31 (br, 1H, outer NH), 8.13 (d, J=2.0 Hz, 1H, αH), 7.94 (d, J=5.0 Hz, 1H, βH), 7.92 (d, J=5.0 Hz, 1H, βH), 7.78 (d, J=5.0 Hz, 1H, βH), 7.76 (d, J=5.0 Hz, 1H, βH), 7.67–7.45 (m, 6H, Ar), 4.44 (q, J=7.5 Hz, 2H, CH$_2$O), 1.25 (t, J=7.5 Hz, 3H, CH$_3$). UV/vis (CHCl$_3$): λ_{max} (nm) 370.0, 444.0, 619.0. FABMS: *m*/*z* (% intensity)=1033.7

(50, M^+), 1035.7 (100, M^++2). Calcd for $C_{46}H_{17}CuCl_4F_{10}N_4O$, 1033.94.

4.3.2. Cu(III) Complex of 2-ethoxy-10,20-bis(2′-nitrophenyl)-5,15-bis(pentafluorophenyl)-3,7-diaza-21,22-dicarbaporphyrin (8-Cu). The mixed solution was stirred at 60 °C for 26 h. Two diastereomeric atropisomers were isolated after the flash silica gel column (CH_2Cl_2). One of the isomers was obtained in 20% yield, but the other was in trace. R_f=0.20 (CH_2Cl_2). ^1H NMR ($CDCl_3$, 500 MHz, 27 °C): δ (ppm) 10.02 (br, 1H, outer NH), 8.36 (dd, *J*=7.5, 2.5 Hz, 1H, *m*-Ar), 8.30 (dd, *J*=7.5, 2.5 Hz, 1H, *m*-Ar), 8.08 (d, *J*=3.5 Hz, 1H, αH), 8.02 (dd, *J*=7.0, 2.0 Hz, 1H, Ar), 7.92 (d, *J*=5.0 Hz, 1H, βH), 7.89–7.86 (m, 2H, Ar), 7.83 (d, *J*=5.0 Hz, 1H, βH), 7.78 (dd, *J*=4.0, 2.0 Hz, 1H, Ar), 7.76 (dd, *J*=4.0, 2.0 Hz, 1H, Ar), 7.73 (d, *J*=5.0 Hz, 2H, βH), 7.67 (dd, *J*=6.5, 4.0 Hz, 1H, Ar), 4.35 (q, *J*=7.0 Hz, 2H, CH_2O), 1.02 (t, *J*=7.0 Hz, 3H, CH_3). UV/vis ($CHCl_3$): λ_{max} (nm) 368.5, 445.0, 624.0. FABMS: *m/z* (% intensity)=988.0 (90, M^+), 989.0 (100, M^++1). Calcd for $C_{46}H_{19}CuF_{10}N_6O_5$, 988.07.

4.3.3. Cu(III) Complex of 2-ethoxy-10,20-bis(3′-nitrophenyl)-5,15-bis(pentafluorophenyl)-3,7-diaza-21,22-dicarbaporphyrin (9-Cu). The mixed solution was stirred at 60 °C for 14 h. In a quantitative yield. R_f=0.12 (CH_2Cl_2). ^1H NMR ($CDCl_3$, 500 MHz, 27 °C): δ (ppm) 10.23 (br, 1H, outer NH), 8.79 (s, 1H, Ar), 8.61 (s, 1H, Ar), 8.57 (d, *J*=10.0 Hz, 1H, Ar), 8.47 (d, *J*=10.0 Hz, 1H, Ar), 8.25 (d, *J*=7.5 Hz, 1H, Ar), 8.24 (br, 1H, αH), 8.09 (d, *J*=5.0 Hz, 1H, βH), 8.05 (d, *J*=7.0 Hz, 1H, Ar), 7.99 (d, *J*=5.0 Hz, 1H, βH), 7.87 (t, *J*=7.5 Hz, 1H, Ar), 7.84 (d, *J*=5.0 Hz, 1H, βH), 7.83 (d, *J*=5.0 Hz, 1H, βH), 7.74 (t, *J*=7.5 Hz, 1H, Ar), 4.38 (q, *J*=7.5 Hz, 2H, CH_2O), 0.99 (t, *J*=7.5 Hz, 3H, CH_3). UV/vis ($CHCl_3$): λ_{max} (nm) 368.0, 444.5, 619.0. FABMS: *m/z* (% intensity)=988.1 (100, M^+). Calcd for $C_{46}H_{19}CuF_{10}N_6O_5$, 988.07.

4.3.4. Cu(III) Complex of 2-ethoxy-10,20-bis(4′-nitrophenyl)-5,15-bis(pentafluorophenyl)-3,7-diaza-21,22-dicarbaporphyrin (10-Cu). In a quantitative yield. R_f=0.38 (CH_2Cl_2). ^1H NMR ($CDCl_3$, 500 MHz, 27 °C): δ (ppm) 10.29 (br, 1H, outer NH), 8.54 (d, *J*=9.0 Hz, 2H, *m*-Ar), 8.44 (d, *J*=9.0 Hz, 2H, *m*-Ar), 8.24 (d, *J*=3.0 Hz, 1H, αH), 8.11 (d, *J*=9.0 Hz, 2H, *o*-Ar), 8.11 (d, *J*=5.0 Hz, 1H, βH), 7.98 (d, *J*=5.0 Hz, 1H, βH), 7.89 (d, *J*=9.0 Hz, 2H, *o*-Ar), 7.85 (d, *J*=5.0 Hz, 1H, βH), 7.83 (d, *J*=5.0 Hz, 1H, βH), 4.41 (q, *J*=7.0 Hz, 2H, CH_2O), 1.02 (t, *J*=7.0 Hz, 3H, CH_3). UV/vis ($CHCl_3$): λ_{max} (nm) 368.0, 447.5, 621.0. FABMS: *m/z* (% intensity)=988.2 (90, M^+), 989.2 (100, M^++1). Calcd for $C_{46}H_{19}CuF_{10}N_6O_5$, 988.07.

4.4. General procedures for Ag(III) complexes of *cis*-doubly N-confused porphyrins (*cis*-N_2CP-Ag)

To a solution of ethoxy substituted tetraaryl-N_2CP (**7-10**) (10.2 mg, 0.01 mmol) in 10 ml of 10% pyridine–$CHCl_3$, AgOAc (8.35 mg, 0.05 mmol) was added and the solution was stirred at room temperature overnight. The solution was filtered through a silica gel column (Wakogel C-200) to remove the excess silver salt and the filtrate was evaporated. Recrystallization from hexane/CH_2Cl_2 gave N_2CP-Ag as a green solid.

4.4.1. Ag(III) Complex of 2-ethoxy-10,20-bis(2′,6′-dichlorophenyl)-5,15-bis(pentafluorophenyl)-3,7-diaza-21,22-dicarbaporphyrin (7-Ag). In a quantitative yield. R_f=0.40 (CH_2Cl_2). ^1H NMR ($CDCl_3$, 500 MHz, 27 °C): δ (ppm) 9.95 (br, 1H, outer NH), 8.09 (d, *J*=3.0 Hz, 1H, αH), 7.86 (d, *J*=5.0 Hz, 1H, βH), 7.85 (d, *J*=5.0 Hz, 1H, βH), 7.71 (d, *J*=5.0 Hz, 2H, βH), 7.67–7.45 (m, 6H, Ar), 4.44 (q, *J*= 7.5 Hz, 2H, CH_2O), 1.08 (t, *J*=7.5 Hz, 3H, CH_3). UV/vis ($CHCl_3$): λ_{max} (nm) 368.0, 443.5, 626.5, 670.5. FABMS: *m/z* (% intensity)=1080.0 (100, M^++2), 1082.0 (95, M^++4). Calcd for $C_{46}H_{17}AgCl_4F_{10}N_4O$, 1077.90.

4.4.2. Ag(III) Complex of 2-ethoxy-10,20-bis(2′-nitrophenyl)-5,15-bis(pentafluorophenyl)-3,7-diaza-21,22-dicarbaporphyrin (8-Ag). The mixture solution was stirred at 60 °C for 12 h. Two diastereomeric atropisomers were isolated after the flash silica gel column (CH_2Cl_2). The products were obtained in 20 (first fraction) and 10% (second fraction) yields, respectively. R_f=0.20 (CH_2Cl_2). ^1H NMR ($CDCl_3$, 500 MHz, 27 °C): δ (ppm) (major isomer) 9.93 (br, 1H, outer NH), 8.35 (dd, *J*=7.5, 1.5 Hz, 1H, *m*-Ar), 8.30 (m, 1H, *m*-Ar), 8.06 (d, *J*=3.0 Hz, 1H, αH), 8.02 (m, 1H, Ar), 7.88–7.86 (m, 2H, Ar), 7.85 (d, *J*=5.0 Hz, 1H, βH), 7.80–7.72 (m, 4H, βH and Ar), 7.68 (d, *J*=5.0 Hz, 1H, βH), 7.66 (d, *J*=4.5 Hz, 1H, βH), 4.36 (q, *J*=7.0 Hz, 2H, CH_2O or CH_3), 1.03 (t, *J*=7.0 Hz, 3H, CH_2O or CH_3); (minor isomer) 9.95 (br, 1H, outer NH), 8.36 (dd, *J*=6.5, 2.0 Hz, 1H, *m*-Ar), 8.31 (dd, *J*=6.5, 2.0 Hz, 1H, *m*-Ar), 8.07 (s, 1H, αH), 7.99 (dd, *J*=5.5, 3.0 Hz, 1H, Ar), 7.87–7.84 (m, 3H, Ar), 7.81 (m, 1H, Ar), 7.77 (d, *J*=4.5 Hz, 2H, βH) 7.72 (dd, *J*=6.5, 3.0 Hz, 1H, Ar), 7.68 (d, *J*=5.0 Hz, 1H, βH), 7.66 (d, *J*=4.5 Hz, 1H, βH), 4.43–4.29 (m, 2H, CH_2O), 1.03 (t, *J*=7.0 Hz, 3H, CH_3). UV/vis ($CHCl_3$): λ_{max} (nm) (major isomer) 367.0, 444.5, 517.5, 630.0, 672.0; (minor isomer) 360.0, 444.5, 516.5, 630.0, 671.5. FABMS: *m/z* (% intensity)=1031.8 (70, M^+), 1032.9 (80, M^++1), 1033.9 (100, M^++1). Calcd for $C_{46}H_{19}AgF_{10}N_6O_5$, 1032.03.

4.4.3. Ag(III) Complex of 2-ethoxy-10,20-bis(3′-nitrophenyl)-5,15-bis(pentafluorophenyl)-3,7-diaza-21,22-dicarbaporphyrin (9-Ag). The mixture solution was stirred at 60 °C for 18 h. In a quantitative yield. R_f=0.16 (CH_2Cl_2). ^1H NMR ($CDCl_3$, 500 MHz, 27 °C): δ (ppm) 10.24 (br, 1H, outer NH), 8.81 (s, 1H, Ar), 8.64 (s, 1H, Ar), 8.56 (dd, 1H, Ar), 8.47 (dd, 1H, Ar), 8.28 (dd, 1H, Ar), 8.22 (d, *J*=2.5 Hz, 1H, αH), 8.08 (dd, 1H, Ar), 8.03 (d, *J*=5.5 Hz, 1H, βH), 7.90 (d, *J*=5.0 Hz, 1H, βH), 7.87 (m, 1H, Ar), 7.81 (d, *J*=5.0 Hz, 1H, βH), 7.77 (d, *J*=5.5 Hz, 1H, βH), 7.75 (m, 1H, Ar), 4.39 (m, 2H, CH_2O), 1.01 (t, *J*=7.0 Hz, 3H, CH_3). UV/vis ($CHCl_3$): λ_{max} (nm) 365.5, 445.0, 515.0, 584.5, 627.5, 671.5. FABMS: *m/z* (% intensity)= 1032.1 (90, M^+), 1034.1 (100, M^++2). Calcd for $C_{46}H_{19}AgF_{10}N_6O_5$, 1032.03.

4.4.4. Ag(III) Complex of 2-ethoxy-10,20-bis(4′-nitrophenyl)-5,15-bis(pentafluorophenyl)-3,7-diaza-21,22-dicarbaporphyrin (10-Ag). The mixture solution was stirred at 60 °C for 18 h. In a quantitative yield. R_f=0.45 (CH_2Cl_2). ^1H NMR ($CDCl_3$, 500 MHz, 27 °C): δ (ppm) 10.26 (br, 1H, outer NH), 8.55 (d, *J*=9.0 Hz, 2H, *m*-Ar), 8.44 (d, *J*=9.0 Hz, 2H, *m*-Ar), 8.23 (d, *J*=3.0 Hz, 1H, αH), 8.13 (d, *J*=9.0 Hz, 2H, *o*-Ar), 8.04 (d, *J*=5.0 Hz, 1H, βH), 7.92 (d, J=9.0 Hz, 2H, o-Ar), 7.88 (d, J=5.0 Hz, 1H, βH), 7.80 (d, J=5.0 Hz, 1H, βH), 7.76 (d, J=5.0 Hz, 1H, βH), 4.41 (q, J=7.0 Hz, 2H, CH_2O), 1.03 (t, J=7.0 Hz, 3H, CH_3). UV/vis ($CHCl_3$): λ_{max} (nm) 367.5, 448.5, 629.5, 671.5. FABMS: m/z (% intensity)=1032.3 (85, M^+), 1034.3 (100, M^++2). Calcd for $C_{46}H_{19}AgF_{10}N_6O_5$, 1032.03.

4.5. 2-Ethoxy-5,15-bis(2′,6′-dichlorophenyl)-10,20-bis-(pentafluorophenyl)-3,7-diaza-21,22-dicarbaporphyrin (11)

N-confused 5-pentafluorophenyldipyrromethane (**1**) (468 mg, 1.5 mmol) and 2,6-dichlorobenzaldehyde (263 mg, 1.5 mmol) were used as starting materials. The green colored product was separated by silica gel column chromatography (CH_2Cl_2/hexane, Wakogel C-200) and thin layer chromatography, followed by recrystallization from hexane/CH_2Cl_2 to give **11** as a green solid in a trace amount. R_f=0.40 (CH_2Cl_2). ^{1}H NMR (CD_2Cl_2, 500 MHz, 27 °C): δ (ppm) 9.00 (br, 1H, outer NH), 7.61–7.47 (m, 8H, Ar), 7.36 (d, J=5.0 Hz, 1H, βH), 7.29 (d, J=5.5 Hz, 1H, βH), 7.03 (s, 1H, αH), 7.02 (d, J=5.5 Hz, 1H, βH), 6.92 (d, J=5.0 Hz, 1H, βH), 6.20 (br, 1H, inner NH), 4.29 (q, J=7.0 Hz, 2H, CH_2O), 3.34 (s, 1H, inner CH), 3.14 (s, 1H, inner CH), 1.10 (t, J=7.0 Hz, 3H, CH_3). UV/vis ($CHCl_3$): λ_{max} (nm) 349.0, 420.5, 629.5, 674.0. FABMS: m/z (% intensity)=974.9 (60, M^++1), 976.0 (100, M^++2). Calcd for $C_{46}H_{20}Cl_4F_{10}N_4O$, 974.02.

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