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One-Step Synthesis and Characterization of Difunctionalized N-Confused Tetraphenylporphyrins

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Three disubstituted N-confused porphyrins (**2**−**4**) were prepared in ca. 4% yield using a one-pot synthesis. These porphyrins bear 3,5-di-*tert*-butylphenyl groups substituted at the C_5 and C_{20} meso positions and para-substituted (Br, NO_2, ethynyl) phenyl groups at the C_{10} and C_{15} meso positions. The specific orientation of the aryl rings around the macrocycle in porphyrin **2** was definitively determined using a combination of 1D (^1H and ^{13}C) and 2D (gHMQC and gHMBC) NMR spectroscopy. The absorption spectra of **2**−**4** in CH_2Cl_2 and dimethylacetamide are similar to those of N-confused tetraphenylporphyrin in the same solvents but have Soret and Q-bands that are shifted to lower energies. Steady-state fluorescence measurements revealed $Q_x(0,0)$ and $Q_x(0,1)$ bands similar in energy to the unsubstituted NCPs **1i** and **1e**. The fluorescence quantum yield results for two of these NCPs (**2**, **4**) are atypical of porphyrin behavior and are being further investigated by time-resolved spectroscopy.

Introduction

The light-harvesting center LHCII[1] in several green plant systems, as well as LH2[2] and LH1[3] in purple bacteria, all utilize various bacteriochlorophyll *a* (BChl*a*, i.e., B800, B850, and B880) pigments arranged in circular arrays. Structural data has led to speculation[4,5] that a combination of hopping and exciton coupling among the BChl*a* pigments is responsible for the efficient electronic energy transfer (EET) within the LH1 and LH2 upon absorption of light. Similarly, the photosynthetic reaction center has evolved over time to facilitate photoinduced electron-transfer (ET) from an electronically excited “special pair” of bacteriochlorophylls to a quinone acceptor.[4] Electron transfer within the reaction center proceeds by a cascade mechanism involving several ultrafast intermediate steps, the high efficiency of which promotes electron-transport over long distances. Successful efforts to mimic both EET within the LHC and ET within the reaction center have used covalently bound[6,7] or supramolecular multiporphyrin arrays.[8−10] Still, the difficulty of preparing chlorins[11,12] and chlorophyll-like structures, and incorporating these compounds into arrays, remains a significant challenge.

N-Confused porphyrins (NCPs) are porphyrin isomers with one of the pyrrolic nitrogens facing outside the macrocycle and one C−H group oriented inward toward

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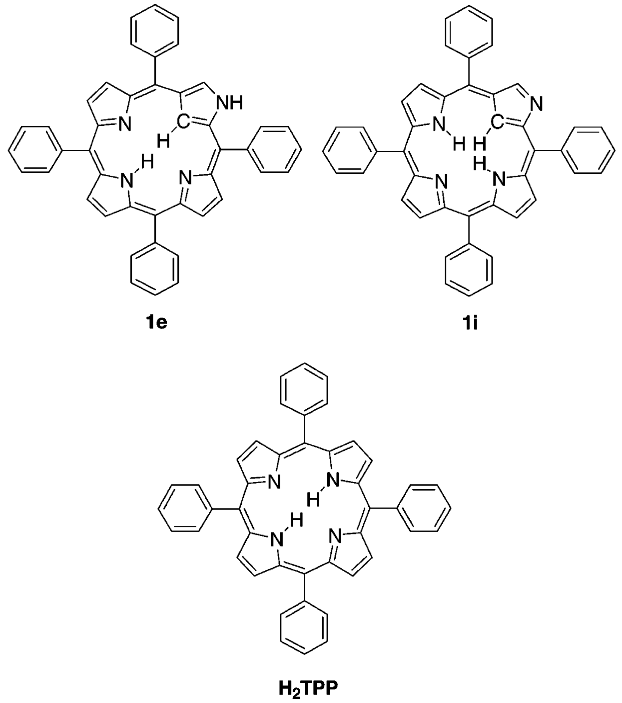

FIGURE 1. Tautomeric forms of N-confused tetraphenyl porphyrin **1e** and **1i** and tetraphenylporphyrin (H_2TPP).

the core. These porphyrins, while differing from the parent tetrapyrrole by the inversion of only two atoms, exhibit physical and chemical properties different from normal porphyrins. Two N-confused porphyrin (NCP) tautomers (Figure 1: **1e**, **1i**) are observed in solution, the polarity of the solvent dictating which tautomer predominates.[13,14] Both tautomers have absorption spectra that are markedly different from that of tetraphenylporphyrin (H_2TPP) and are characterized by Soret and Q-bands that are significantly red-shifted to lower energies.[13,14] The red-shifted absorption maxima are attributed to a break in the degeneracy of the e_g orbitals that results from a decrease in symmetry within the macrocycle.[14] The excited-state properties of each tautomer are different from one another, with **1i** exhibiting a lower excited-state energy and fluorescence quantum yield than tautomer **1e**. The fluorescence lifetimes of both tautomers are comparable.[14]

The aforementioned photophysical properties of N-confused porphyrins, on the other hand, compare favorably to both chlorophylls[15,16] and porphyrins,[17] and because of the low energy absorption bands, represent a viable alternative to porphyrins and the difficult to prepare synthetic chlorins[11] in artificial light-harvesting systems and photonic arrays.[18−20] Nonetheless, incorporation of these porphyrins into devices and arrays has been limited by the ability to readily synthesize functionalized NCPs. Tetrasubstituted N-confused porphyrins can be routinely prepared in high yields by Lindsey's method,[21] but this synthetic route has not yet been applied to mono- or disubstituted N-confused porphyrins. Recently, the synthesis of a disubstituted N-confused 5,20-diphenylporphyrin was described using the 3 + 1 cyclization of tripyrrane with 2,4-bis(phenylhydroxymethyl)pyrrole.[22] The fact that only highly asymmetric 5,20-disubstituted asymmetric porphyrins can be prepared by this method indicates an alternative synthetic route to difunctionalized NCP derivatives might prove useful. In this paper, we report the one-step synthesis of three 10,15-disubstituted NCPs (**2**−**4**, Figure 2) from typical porphyrin precursors.

Results and Discussion

Synthesis. N-Confused porphyrins **2**−**4** were prepared by reacting 0.5 equiv of 3,5-di-*tert*-butylbenzaldehyde and

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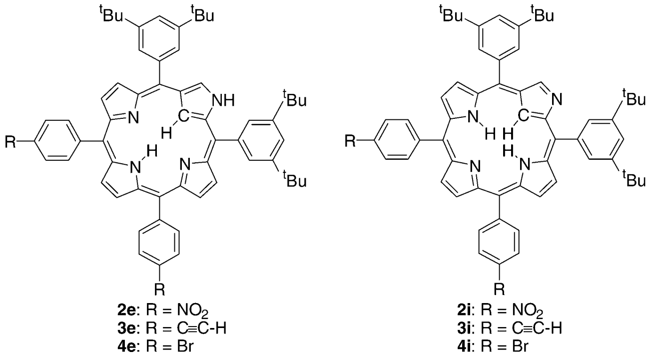
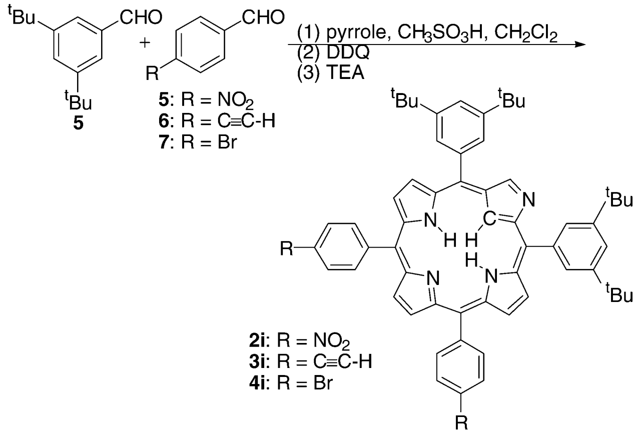


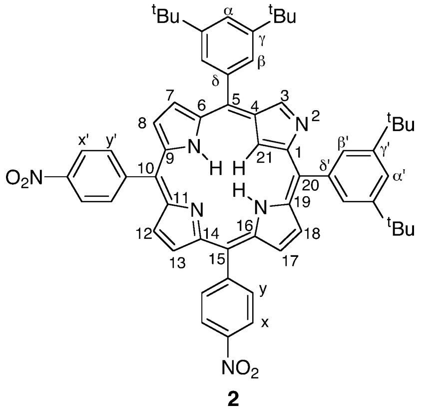
FIGURE 2. Tautomeric forms of N-confused porphyrins **2**−**4**.

SCHEME 1. Synthesis of N-Confused Porphyrins 2−4



0.5 equiv of the appropriate para-substituted benzaldehyde (**5**−**7**) in the presence of 1 equiv of pyrrole and 0.7 equiv of methanesulfonic acid for 30 min (Scheme 1). Oxidation with DDQ afforded a variety of N-confused and regular porphyrins. Isolation of the desired NCP in ~4% yield was accomplished by column chromatography of the products on silica gel and basic alumina.[23] The presence of the 3,5-di-*tert*-butyl substituent on the 5,20-*meso*-phenyl groups was found to be important to the separation of the desired NCP from other N-confused porphyrins. An isomeric NCP (possibly the 10,20-difunctionalized isomer) was formed in <1% yield in these reactions and could be isolated during purification, but was not positively identified. The reason for the apparent preference of the 10,15 isomer is not clear at this time but may be related to a templating effect of the catalyst during the synthesis.[13b] NCPs **2**−**4** were subsequently identified by NMR, UV−vis, and high-resolution TOF-ESI-MS.

NMR Analysis. The substitution pattern of N-confused porphyrin **2** was characterized with the help of both 1D (^{1}H and ^{13}C) and 2D gradient-assisted heteronuclear multiple quantum coherence[24] (gHMQC) and gradient-assisted heteronuclear multiple bond correlation[25] (gHMBC) NMR. A summary of the relevant correlations follows, with a full interpretation of the NMR data provided in the Supporting Information. All the porphyrin and phenyl resonances except the inner C−H and N−H resonances which appear at −2.2 and −4.7 ppm, respectively, were assigned from the aromatic region of the ^{1}H spectrum of **2**. The ^{13}C spectrum of **2** obtained at 100 MHz shows a number of resonances between 100 and 160 ppm, which can only be unambiguously assigned with the help of 2D ^{1}H−^{13}C correlation experiments. One-bond ^{1}H−^{13}C correlations were obtained from the gHMQC experiment in order to identify the proton bearing carbons of the molecule. Although the gHMQC spectrum provides assignments of the proton-bearing carbon resonances, it is insufficient to determine the substitution pattern of the porphyrin ring itself, and multiple bond C−H correlations are necessary to fully identify the structure. In the gHMBC experiment, a delay of $^1/_2J_{CH}$ (based on $J_{CH} = 8$ Hz) was used to optimize the intensities of cross-peaks from three bond ^{1}H−^{13}C couplings. Correlations from other types of couplings also appear but are weak in intensity. The resonance H_β shows a very strong multiple bond correlation with the carbon at 128.6 ppm, which is the point of attachment of the aryl ring to the macrocycle. The same carbon resonance also shows HMBC correlation with the resonances of H_{21} and H_7. This carbon is three bonds away from C_β, C_{21}, and C_7 and must be C_5. Thus, the 3,5-di-*tert*-butylphenyl ring is attached to **2** at C_5. Similarly, $H_{\beta'}$ exhibits a high-intensity cross-peak with the porphyrin ring carbon to which the phenyl ring is attached. As in the case of H_β, the resonance from this carbon at 131.0 ppm also shows HMBC correlations with the resonances of C_{21} and C_{18} and so must be C_{20}, proving the second 3,5-di-*tert*-butylphenyl ring is attached to **2** at C_{20}. The point of attachment of the 4-nitrophenyl groups can be proven by the H_y−C_{15} and $H_{y'}$−C_{10} HMBC correlations. Our assignments are also corroborated from the single and multiple bond correlations of the inner H_{21} resonance.



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Absorption Spectroscopy. The absorption spectra of N-confused porphyrins **1i** and **1e** are characterized by significantly red-shifted Soret and Q-band absorptions[13] and a marked increase in the oscillator strength of the $Q_x(0,0)$ band.[14] The Soret and Q-bands for **2**−**4** are similarly shifted (Table 1, Figure 3), although to lower energies than observed for **1i** and **1e**. The decrease in the Soret and Q-band energies observed in the absorption spectra can be attributed to a combination of steric[26] effects from the C_5/C_{20} *tert*-butyl phenyl groups and electronic contributions from the para substituents on the

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(23) Complete chromatographic details are provided in the Supporting Information.

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TABLE 1. Summary of Absorption Data for N-Confused Porphyrins 1−4 in CH_2Cl_2 and Dimethylacetamide (DMAc)

compound	solvent	Soret (nm) ($\epsilon \times 10^4$ M^{-1} cm^{-1})	Q-bands (nm) ($\epsilon \times 10^3$ M^{-1} cm^{-1})			
H_2TPP	CH_2Cl_2	417 (54.2)	514 (22.1)	550 (9.22)	590 (6.63)	646 (4.67)
H_2TPP^a	DMAc	417 (48.5)	513 (20.8)	548 (9.67)	591 (6.69)	646 (6.05)
1i	CH_2Cl_2	438 (19.1)	540 (11.9)	582 (14.1)	673 (2.36)	726 (13.3)
1e	DMAc	442 (11.9)	550 (2.0)	595 (6.1)	644 (9.5)	699 (12.4)
2i	CH_2Cl_2	444 (25.6)	546 (13.1)	589 (24.0)	665 (4.3)	726 (19.5)
2e	DMAc	447 (14.0)	546 (6.9)	597 (10.0)	646 (15.1)	701 (20.6)
3i	CH_2Cl_2	441 (17.5)	544 (7.3)	586 (12.0)	671 (1.9)	727 (9.8)
3e	DMAc	445 (8.70)	553 (2.4)	598 (4.9)	646 (6.8)	703 (8.8)
4i	CH_2Cl_2	440 (21.9)	543 (9.0)	585 (15.0)	669 (2.6)	726 (12.8)
4e	DMAc	445 (9.50)	546 (2.3)	596 (4.8)	646 (7.2)	702 (9.2)

[a] Taken from Datta-Gupta, N.; Malakar, D.; Rice, L.; Rivers, S. *J. Heterocycl. Chem.* **1987**, *24*, 629−632.

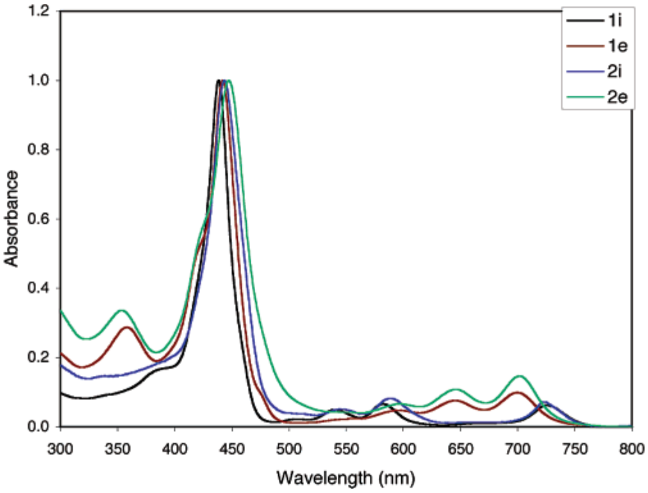

FIGURE 3. Absorption spectra of **1i** (black), **1e** (red), **2i** (blue), and **2e** (green) in CH_2Cl_2 and dimethylacetamide. The spectra have been normalized to the Soret band.

C_{10}/C_{15} phenyl groups.[27,28] General trends in the extinction coefficients of N-confused porphyrins **2**−**4** are consistent with those of **1i** and **1e**,[13,14] with the Soret bands of **2i**−**4i** more intense than those of **2e**−**4e** (Table 1). Similarly, the Q-band extinction coefficients of **2i**−**4i** are all larger than those observed for **2e**−**4e**, with the exception of that of $Q_x(1,0)$.

Fluorescence Spectroscopy. The fluorescence spectra[14] of N-confused porphyrins **1i** and **1e** are characterized by emission bands that are red-shifted from those of H_2TPP and have larger Stokes shifts (Table 2). Tautomer **1e** has a quantum yield of fluorescence (Φ_{Fl}) that is a factor of 2 greater than tautomer **1i** (Φ_{Fl} = 0.0460 vs Φ_{Fl} = 0.0227, respectively)[29] and has a fluorescence lifetime that is slightly longer-lived (i.e., 1.98 ns vs 1.60 ns, respectively). These minor differences have been attributed[14] to a slightly more rapid rate of internal conversion or intersystem crossing in **1i** that result from unfavorable steric conditions in the interior of the macrocycle.

TABLE 2. Summary of Fluorescence Data for N-confused Porphyrins 1−4 and H_2Br_4NCTPP, Porphyrins H_2Br_4TPP and H_2TPP, and Chlorin H_2TPChl

compd	solvent	fluorescence maxim[a]a (nm)		Φ_{FL}[b]	Stokes shift (cm^{-1})
H_2TPP	CH_2Cl_2	651	715	0.11[c]	143
H_2TPP	DMAc	650	715	0.15[d]	95
1i	CH_2Cl_2	744	815	0.0227	371
1e	DMAc	713	783	0.0460	281
2i	CH_2Cl_2	741	817	0.0263	279
2e	DMAc	717	795	0.0240	318
3i	CH_2Cl_2	744	817	0.0269	314
3e	DMAc	718	798	0.0578	297
4i	CH_2Cl_2	741	818	0.0127	279
4e	DMAc	716	795	0.0453	279
$H_2Br_4NCTPPi$	CH_2Cl_2	744	818	0.00497	295
$H_2Br_4NCTPPe$	DMAc	713	795	0.0201	281
H_2Br_4TPP	CH_2Cl_2	649	714	0.0138	96
H_2Br_4TPP	DMAc	649	714	0.0153	96
H_2TPChl	C_6H_6	660	730[e]		233

[a] Excited at the Soret bands to avoid aggregation due to concentration effects. [b] Relative to the fluorescence of H_2TPP. Quantum yields were calculated using standard methods. [c] Seybold, P. G.; Gouterman, M. *J. Mol. Spectrosc.* **1969**, *31*, 1−13. [d] See ref 28. [e] Taken from ref 13b.

Steady-state fluorescence data for disubstituted NCPs **2**−**4** are tabulated in Table 2. Consistent with the red-shifts in the absorption spectra, the fluorescence spectra of **2**−**4** have emission bands that are significantly red-shifted relative to those of H_2TPP. The fluorescence spectra of **2**−**4** are dominated by large $Q_x(0,0)$ emission bands at ~741−744 nm (in CH_2Cl_2) and ~716−718 nm (in DMAc). Smaller low energy $Q_x(0,1)$ shoulders are observed at ~817−818 nm (CH_2Cl_2) and ~795−798 nm (DMAc). The ratios of the areas of the $Q_x(0,0)$ and $Q_x(0,1)$ emission bands are significantly larger than those of H_2TPP and are similar to the ratios for the NCP $Q_x(0,0)$ and $Q_x(1,0)$ absorption bands. These differences have previously been attributed to changes in the ground-state ↔ Q-state excited-state transitions.[14]

Minor differences among NCPs **2**−**4** are evident from the fluorescence quantum yield data. In general, the fluorescence quantum yield values are slightly larger in the more polar solvent DMAc than in CH_2Cl_2. These results are consistent with a more rapid decay of the excited state in **2i**−**4i** by a nonradiative mechanism that is facilitated by the increased steric congestion in these

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(26) The absorption spectrum of 5,10,15,20-tetrakis(3,5-di-*tert*-butylphenyl) N-confused porphyrin (H_2Bu_8NCTPP) has a Soret band at 441 nm in CH_2Cl_2 and 445 nm in DMAc; see the Supporting Information.

(27) The absorption spectrum of 5,10,15,20-tetrakis(4-bromophenyl) N-confused porphyrin has a red-shifted Soret band at 441 nm in CH_2Cl_2 and 452 nm in DMAc; see the Supporting Information.

(28) Kim, J. B.; Leonard, J. L.; Longo, F. R. *J. Am. Chem. Soc.* **1972**, *94*, 3986−3992. Harriman, A.; Hosie, R. J. *J. Chem. Soc., Faraday Trans. 2* **1981**, 77, 1695−1702.

(29) It should be noted that the values reported here are different than those reported by us earlier (see ref 14) and should be considered more accurate and precise.

tautomers.[14] The exception to this generalization is **2e**, for which Φ_{Fl} is nearly identical to **2i**. Semiempirical (PM3) calculations reveal a much larger dipole in **2e** (13.4 D) compared to **2i** (7.2 D), **4e** (6.4 D), or **1e** (4.3 D), indicating the nitro groups on the more planar **2e** may have charge-transfer character that accelerates decay of the S_1 state. Time-resolved experiments are underway to further investigate these results.

The presence of bromine is known to decrease the fluorescence quantum yields of organic compounds through the heavy atom effect.[30] For example, the Φ_{Fl} value for H_2TPP is 1 order of magnitude greater than the analogous value for 5,10,15,20-tetrakis(4-bromophenyl)porphyrin (H_2Br_4TPP, Table 2). Based upon these data, NCPs **4i** and **4e** were therefore expected to have Φ_{Fl} values that were substantially smaller than **1**−**3**. However, the fluorescence quantum yield of **4i** is smaller than that of **1i** only by a factor of 2, and the quantum yield of **4e** is identical within experimental error to that of **1e**. To help explain these unusual results, the fluorescence spectra of 5,10,15,20-tetrakis(4-bromophenyl) N-confused porphyrin (**H_2Br_4NCTPP**) in CH_2Cl_2 and DMAc were compared to the spectra of **1i** and **1e**. The Φ_{Fl} value of **H_2Br_4NCTPP** in CH_2Cl_2 is 1 order of magnitude smaller than that of **1i**, similar to the fluorescence data for H_2TPP and H_2Br_4TPP; however, Φ_{Fl} for **H_2Br_4NCTPP** in DMAc is smaller than **1e** by only a factor of 2. Examination of the orbital occupancies and energies in these porphyrins indicates only minor differences between the differently substituted NCPs within each series of tautomer (i.e., **2i**−**4i** and **H_2Br_4NCTPPi**; **2e**−**4e** and **H_2Br_4NCTPPe**), and cannot be used to explain the differences in Φ_{Fl} observed in the brominated porphyrins. Similarly, structural differences between the disubstituted NCPs (and **H_2Br_4NCTPP**) are minor, with **2i**−**4i** and **H_2Br_4NCTPPi** all having saddle-type deformations in the macrocycle[14,31] and **2e**−**4e** and **H_2Br_4NCTPPe** having largely planar macrocycles. The two sets of data are self-consistent, but do not answer the larger question of the origin of the larger-than-expected Φ_{Fl} values. Time-resolved experiments are currently being performed to elucidate the nature of this interesting excited-state energy surface.

Conclusions. A series of disubstituted N-confused porphyrins has been synthesized and the structure of one of these porphyrins is definitively identified using 1D and 2D NMR spectroscopies. The absorption spectra of these NCPs are consistent with unsubstituted NCPs **1i** and **1e** but have red-shifted Soret and Q-bands. Steady-state fluorescence spectroscopy reveals $Q_x(0,0)$ and $Q_x(0,1)$ bands similar in energy to the unsubstituted NCPs **1i** and **1e**. The fluorescence quantum yield results for two of these NCPs (**2**, **4**) are atypical of porphyrin behavior in general, and are being further investigated by time-resolved spectroscopy.

Experimental Section

General Method for 10,15-Disubstituted N-Confused Porphyrins. In a 1 L round-bottom three-neck flask were dissolved the para-substituted benzaldehyde (3.0 mmol), 3,5-di-*tert*-butylbenzaldehyde[32] (3.0 mmol), and pyrrole (6.0 mmol) in 600 mL of dichloromethane. Methanesulfonic acid (4.2 mmol, 0.27 mL) was then added slowly, and the reaction was allowed to stir for 30 min. DDQ (5.3 mmol, 1.2 g) was added all at once and the reaction stirred for 10 min more and then quenched with triethylamine (2.0 mL). The crude mixture was filtered through activity III basic alumina (200 g), flushed with a solution of CH_2Cl_2/TEA (99:1), and concentrated under vacuum. Column chromatography on silica using 100% CH_2Cl_2 removed the porphyrin isomers. Gradual additions of methanol to the eluent yielded the isolation of the retained N-confused isomers.

Synthesis of 5,20-Bis(3,5-di-*tert*-butylphenyl)-10,15-bis-(4-nitrophenyl) N-Confused Porphyrin (2). N-Confused porphyrin **2** was further purified by column chromatography on activity III basic alumina (70:30 hexanes/CH_2Cl_2 to 50:50 hexanes/CH_2Cl_2) followed by recrystallization from CH_2Cl_2 and CH_3CN to yield a purplish solid (55.7 mg, 4%): ^{1}H NMR (300 MHz, $CDCl_3$, δ) −4.78 (s, 1H), −2.26 (bs, 2H), 1.60 (d, 36 H, J = 2.5 Hz), 7.89 (d, 2H, J = 4.9 Hz), 8.24 (d, 4H, J = 8.5 Hz), 8.40 (m, 4H), 8.54 (m, 4H), 8.68 (d, 4H, J = 8.5 Hz), 8.75 (s, 1H), 8.99 (d, 1H, J = 4.8 Hz), 9.09 (d, 1H, 5.1 Hz); ^{13}C NMR (75 MHz, $CDCl_3$, δ) 32.0, 35.4, 101.0, 114.5, 116.0, 122.5, 122.5, 122.7, 122.8, 124.3, 125.5, 128.6, 129.2, 129.5, 131.0, 132.5, 132.8, 134.4, 134.9, 135.2, 135.5, 135.5, 137.7, 138.1, 138.8, 138.9, 139.6, 148.0, 148.9, 149.0, 149.5, 150.4, 150.6, 155.4, 156.3, 156.6; TOF-MS (ES$^+$) $C_{60}H_{60}N_6O_4$ calcd m/z 929.4754, obsd m/z 929.4754 [M]H$^+$; UV−vis (λ_{max}, nm, CH_2Cl_2) 447, 546, 597, 646, 701.

Synthesis of 5,20-Bis(3,5-di-*tert*-butylphenyl)-10,15-bis-(4-ethynylphenyl) N-Confused Porphyrin (3).[33] Column chromatography of the isomeric product mixture on activity III basic alumina (98:2 hexanes/EtOAc) followed by recrystallization from CH_2Cl_2 and CH_3CN yielded a purplish solid (53.3 mg, 4%): ^{1}H NMR (300 MHz, $CDCl_3$, δ) −4.91 (s, 1H), −2.33 (bs, 2H), 1.60 (d, 36H, J = 3.7 Hz), 3.32 (s, 2H), 7.83 (d, 2H, J = 7.3 Hz), 7.89 (d, 4H, J = 7.3 Hz), 8.19 (m, 8H), 8.56 (m, 4H), 8.74 (s, 1H), 8.92 (d, 1H, J = 4.9 Hz), 9.02 (d, 1H, J = 5.4 Hz); ^{13}C NMR (75 MHz, $CDCl_3$, δ) 32.0, 35.4, 78.0, 78.5, 83.8, 99.9, 122.3, 122.5, 125.3, 125.9, 128.6, 128.9, 129.9, 131.0, 132.4, 132.6, 134.5, 134.8, 135.0, 139.1, 142.8, 149.3, 150.2, 156.3; TOF-MS (ES$^+$) $C_{64}H_{62}N_4$ calcd m/z 887.5052, obsd m/z 887.5045 [M]H$^+$; UV−vis (λ_{max}, nm, CH_2Cl_2) 445, 553, 598, 646, 704.

Synthesis of 5,20-Bis(3,5-di-*tert*-butylphenyl)-10,15-bis-(4-bromophenyl) N-Confused Porphyrin (4). Column chromatography of the isomeric product mixture on activity III basic alumina (98:2 hexanes/EtOAc) followed by further separation by column chromatography on activity III basic alumina (70:30 hexanes/CH_2Cl_2) and recrystallization from CH_2Cl_2 and CH_3CN yielded a purplish solid (59.8 mg, 4%): ^{1}H NMR (300 MHz, $CDCl_3$, δ) −4.93 (s, 1H), −2.38 (bs, 2H), 1.60 (d, 36 H, J = 3.1 Hz), 7.84 (d, 2H, 8.5 Hz), 7.90 (d, 4H, J = 7.3 Hz), 8.06 (m, 4H), 8.21 (d, 4H, J = 15.9 Hz), 8.74 (s, 1H), 8.93 (d, 1H, J = 4.9 Hz), 9.03 (d, 1H, J = 4.9 Hz); ^{13}C NMR (75 MHz, $CDCl_3$, δ) 32.0, 35.4, 100.0, 113.2, 122.3, 122.5, 125.2, 125.9, 128.6, 128.9, 130.4, 132.4, 132.6, 134.5, 134.9, 136.1, 136.2, 137.6, 139.1, 139.4, 140.0, 141.1, 149.3, 150.2, 156.3; TOF-MS (ES$^+$) $C_{60}H_{60}N_4Br_2$ calcd m/z 997.3246, obsd m/z 997.3234 [M]H$^+$; UV−vis (λ_{max}, nm, CH_2Cl_2) 445, 546, 596, 646, 702.

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Supporting Information Available: Characterization (^{1}H and ^{13}C NMR, TOF-MS data) of N-confused porphyrins **2**−**4**, synthetic procedures for the preparation of H_2Bu_8NCTPP and H_2Br_4NCTPP, and detailed 1D- and 2D-NMR analysis of **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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