Supporting information for:

Facile Peripheral Modification of N-confused Porphyrin

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General Experimental Methods. Instrumentation: All ^1H and ^{13}C NMR spectra were recorded on Varian VXR or GEMINI spectrometers at 300 MHz and 75 MHz in CDCl_3 , respectively. The CDCl_3 peak was used as an internal standard (7.27 ppm for ^1H and 77.23 ppm for ^{13}C). ^1H - ^{13}C 2D HETCOR spectra were recorded on a Varian INOVA 400 spectrometer. Absorption experiments were carried out on a Hitachi 3310 single monochromator spectrophotometer, and dichloromethane was chosen as the solvent. High resolution mass spectrometry experiments were performed on a Micromass ESI-ToFTM II (Micromass, Wythenshawe, UK) mass spectrometer equipped with an orthogonal electrospray source (Z-spray) operated in positive ion mode. Sodium iodide was used for mass calibration for a calibration range of m/z 100-2000. Samples were prepared in a solution containing acidified methanol and infused into the electrospray source at a rate of 5-10 $\mu\text{l min}^{-1}$. Optimal ESI conditions were: capillary voltage 3000 V, source temperature 110°C and a cone voltage of 55 V. The ESI gas was nitrogen. Data was acquired in continuum mode until acceptable averaged data was obtained. X-ray intensity data were measured at 100 K (Bruker KYRO-FLEX) on a Bruker SMART APEX CCD-based X-ray diffractometer system equipped with a Mo-target X-ray tube ($\lambda = 0.71073 \text{ \AA}$) operated at 2000 W power. The crystal was mounted on a cryoloop using Fomblin oil and placed under a stream of nitrogen at 100 K. The detector was placed at a distance of 5.009 cm from the crystal.

Materials: All chemicals were purchased from Sigma-Aldrich or Lancaster. THF was distilled from sodium-benzophenone ketyl, and other solvents were distilled from CaH_2 before use. Basic and neutral alumina gel for flash chromatography (50-200 μm) was obtained from ACROS Organics or Sorbent Technologies. Alumina neutral TLC plates (200 μm) were purchased from Sorbent Technologies.

Preparation of the Precursors:

5,10,15,20-Tetraphenyl N-confused porphyrin: This compound was prepared according to Lindsey's modified procedure.¹ Preparation of the precursor

¹ Geier III, G. R.; Haynes, D. M.; Lindsey, J. S. *Org. Lett.* **1999**, *1*, 1455-1458.

2-bromo-N,N-diethylacetamide **2c**: Following the previous report,²³ diethylamine 0.82 mL (7.9 mmol) dissolved in 5 mL CH₂Cl₂ was slowly added to a solution of bromoacetyl chloride 621 mg (3.95 mmol) in 5 mL CH₂Cl₂ at -78°C. The reaction mixture was then left to warm to room temperature. The reaction mixture was poured into 20 mL H₂O and extracted with 3 × 20 mL CHCl₃. The combined extract was dried over anhydrous Na₂SO₄, filtered and concentrated. After confirmation by ¹H NMR, this compound was used in the following N-alkylation reaction without further purification. ¹H NMR (300MHz, CDCl₃): δ 1.15 (t, 7.1 Hz, 3H), 1.26 (t, 7.1 Hz, 3H), 3.40 (q, 7.1 Hz, 4H), 3.85 (s, 2H).

Synthesis of N-alkylated N-confused porphyrin Co-3a metal complex: Under anaerobic conditions, **3a** was refluxed with a slight excess of Co₂(CO)₈ in toluene. After one hour the reaction was completed. Evaporation of toluene under reduced pressure followed by filtration with a heptane wash yielded the crude metalloporphyrin in quantitative yield. Crystallization from pyridine/heptane produced x-ray quality crystals of **Co-3a**.

Spectroscopic Data:

5,10,15,20-tetraphenyl N-confused porphyrin—methylbenzoate (3b): Followed the procedure 2 described in the experimental section, general procedure, 61 mg (0.1 mmol) NCTPP **1**, 46 mg (0.2 mmol) methyl (4-bromomethyl)benzoate **2b**, 49 mg (0.15 mmol) Cs₂CO₃, and 5 mL THF and 0.2 mL DMSO mixture were used for reaction, 33 mg (43.0%) dark green crystalline solid product **3b** was obtained. ¹H NMR (300 MHz, CDCl₃): δ 7.98-7.93 (m, 2H), 7.91 (d, J = 4.7 Hz, 1H), 7.63-7.54 (m, 15H), 7.55 (d, J = 4.6 Hz, 1H), 7.46 (d, J = 7.4 Hz, 2H), 7.38-7.37 (m, 2H), 6.42 (d, J = 8.0 Hz, 2H), 5.05 (s, 2H), 4.08 (b, 1H), 3.80 (s, 3H), 1.81 (s, 1H); ¹³C NMR (75 MHz, CDCl₃): δ 166.7, 164.1, 163.8, 155.0, 154.2, 144.1, 143.8, 142.7, 141.8, 141.7, 141.3, 140.1, 136.6, 136.2, 135.4, 135.2, 135.0, 133.7, 133.5, 133.3, 131.2, 131.1, 130.8, 129.8, 129.7, 129.5, 129.4, 128.5, 128.3, 128.0, 127.7, 127.5, 127.4, 127.0, 125.7, 124.5, 116.0,

² Jozua F. Booysen, Cedric W. Holzapfel. *Synth. Comm.* **1995**, 25, 1461-1472.

³ Takuo, Hama, Xiaoxiang Liu, Darcy A. Culkin, John F. Hartwig. *J. Am. Chem. Soc.* **2003**, 125, 1176-1177.

115.7, 108.0, 54.0, 52.2; UV/Vis(CH₂Cl₂): λ_{max} (ϵ) 360 (401640), 447 (1043800), 658 (95375), 717 (125050), 823 (66762); MS(ESI) Calc for C₅₃H₃₉N₄O₂ ([M+H]⁺) 763.9, found 763.2; HRMS(ESI) Calc for C₅₃H₃₉N₄O₂ ([M+H]⁺) 763.3073, found 763.3046.

5,10,15,20-tetraphenyl N-confused porphyrin—amide (3c):

Followed the procedure 2 described in the experimental section, general procedure, 61 mg (0.1 mmol) NCTPP **1**, 78 mg (0.4 mmol) 2-bromo-N,N-diethylacetamide **2c**, 98 mg (0.3 mmol) Cs₂CO₃, and 5 mL THF and 0.2 mL DMSO mixture were used for reaction, 51 mg (69.6%) dark green crystalline solid product **3c** was obtained. ¹H NMR (300 MHz, CDCl₃): δ 8.04-7.96 (m, 4H), 7.87 (bs, 4H), 7.76 (bs, 3H), 7.64-7.60 (m, 10H), 7.53 (d, J = 4.4 Hz, 1H), 7.47 (d, J = 4.3 Hz, 1H), 7.39 (s, 3H), 7.37 (s, 1H), 4.53 (s, 2H), 3.91 (b, 1H), 3.29 (q, J = 7.0 Hz, 2H), 2.66 (q, J = 7.0 Hz, 2H), 1.39 (s, 1H), 1.11 (t, J = 7.0 Hz, 3H), 0.89 (t, J = 7.0 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃): δ 165.3, 163.7, 163.2, 154.9, 154.0, 143.8, 143.3, 141.8, 141.4, 140.7, 138.0, 137.0, 135.5, 135.2, 134.9, 133.8, 133.7, 133.6, 131.6, 131.3, 131.0, 130.6, 129.5, 129.2, 128.3, 128.2, 128.0, 127.4, 127.0, 124.8, 116.0, 115.5, 106.0, 50.7, 41.2, 40.8, 14.0, 12.9; UV/Vis(CH₂Cl₂): λ_{max} (ϵ) 362 (42972), 447 (108694), 657 (10237), 714 (13649), 789 (5940); MS(ESI) Calc for C₅₀H₄₂N₅O ([M+H]⁺) 727.9, found 728.2; HRMS(ESI) Calc for C₅₀H₄₂N₅O ([M+Na]⁺) 750.3209, found 750.3201.

Allyl-5,10,15,20-tetraphenyl N-confused porphyrin (3d): Followed the procedure 2 described in the experimental section, general procedure, 61 mg (0.1 mmol) NCTPP **1**, 0.036 mL (0.4 mmol) allylbromide **2d**, 98 mg (0.3 mmol) Cs₂CO₃, and 5 mL THF and 0.2 mL DMSO mixture were used for reaction, 40 mg (61.2%) dark green crystalline solid product **3d** was purified out by flash chromatography. ¹H NMR (300 MHz, CDCl₃): δ 7.98-7.94 (m, 3H), 8.78-7.82 (m, 4H), 7.75-7.71 (m, 2H), 7.65-7.58 (m, 14H), 7.52 (d, J = 4.3 Hz, 1H), 7.47 (d, J = 4.3 Hz, 1H), 7.38 (s, 1H), 7.26 (s, 1H), 5.47 (m, 1H), 4.85 (d, J = 10.2 Hz, 1H), 4.63 (d, J = 17.1 Hz, 1H), 4.29 (d, J = 4.8 Hz, 2H), 1.28 (s, 1H); ¹³C NMR (75 MHz, CDCl₃): δ 141.85, 141.81 split, 141.3, 140.5, 138.8, 136.9, 136.6, 135.3, 134.9, 133.8, 133.6, 133.5, 131.3, 131.0, 130.5, 129.8, 129.5, 129.2, 128.9, 128.6, 128.5, 128.3, 128.2, 128.1, 127.9, 127.4, 127.0, 124.6, 118.0, 116.1, 115.6, 52.9; UV/Vis(CH₂Cl₂): λ_{max} (ϵ) 362 (22597), 449 (62528), 658 (4750),

717 (6548), 814 (5071); MS(ESI) Calc for $C_{47}H_{35}N_4([M+H]^+)$ 655.8, found 655.2; HRMS(ESI) Calc for $C_{47}H_{35}N_4([M+H]^+)$ 655.2861, found 655.2832.

Propyl-5,10,15,20-tetraphenyl N-confused porphyrin (3e): Followed the procedure B described in the experimental section, general procedure, 61 mg (0.1 mmol) NCTPP **1**, 0.04 mL (0.4 mmol) allylbromide **2e**, 98 mg (0.3 mmol) CS_2CO_3 , and 5 mL THF and 0.2 mL DMSO mixture were used for reaction. 53 mg (80.7%) dark green crystalline solid product **3e** was purified out by flash chromatography.

1H NMR (300 MHz, $CDCl_3$): δ 8.00-7.93 (m, 5H), 7.86-7.82 (m, 5H), 7.76-7.72 (m, 2H), 7.66-7.58 (m, 13H), 7.52 (d, $J = 4.7$ Hz, 1H), 7.47 (d, $J = 4.7$ Hz, 1H), 7.38 (s, 2H), 3.76 (b, 1H), 3.59 (t, $J = 7.8$ Hz, 2H), 1.34 (sextet, $J = 7.6$ Hz, 2H), 1.25 (s, 1H), 0.42 (t, $J = 7.3$ Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 200.7, 197.2, 179.4, 163.6, 163.2, 154.6, 153.8, 143.8, 143.3, 142.0, 141.9, 141.5, 140.6, 136.6, 135.8, 135.2, 135.0, 133.8, 133.7, 133.6, 131.0, 130.8, 130.6, 129.5, 129.2, 128.5, 128.4, 127.9, 127.8, 127.4, 127.3, 126.9, 124.2, 115.9, 115.5, 106.7, 52.5, 25.8, 11.2; UV/Vis(CH_2Cl_2): λ_{max} (ϵ) 363 (47011), 448 (125408), 656 (11918), 713 (15891), 817 (4502); MS(ESI) Calc for $C_{47}H_{37}N_4([M+H]^+)$ 657.8, found 657.2; HRMS(ESI) Calc for $C_{47}H_{37}N_4([M+H]^+)$ 657.3018, found 657.3019. Crystallization from a slow diffusion of n-hexane into a **3e** CH_2Cl_2 solution produced x-ray quality crystals of **3e**.

Co-3a: UV/Vis(CH_2Cl_2): λ_{max} (ϵ) 378 (20187), 423 (29683), 607 (3115), 668 (3091), 703 (3161).

NMR spectra of **3a-3e**

Figure 1 ^1H NMR of **3a**

Figure 2 ^{13}C NMR of **3a**

HETCOR E369-MCPethylester-H1aC13
in CDCl3 400 MHz
08/04/05

exp5 hetcor

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data      Aug 5 2005      dfrq      399.804
solvent    CDCl3          da          81
file /home/wj2/HET-      dpr          37
CORR369MCPethylester-    dof      -212.4
                                rny
ACQUISITION      dmp      11857
sfrq      100.539      dmf      11857
ca          C13      dseq      waltz16
at          0.150      dres          n
np          5428      homo          n
sv          18091.4      temp      30.0
zb          not used
ds          16          sb          0.051
ss          1          sbx          0.004
tpr          52          wfile
rv          8.4          wproc          ft
dl          1.000          in          4096
toof      -508.0          math          f
nt          32          werr oreact('wait-
                                ')
alock          n          wexp          procploc
gain          140.0          wba
lsh          0          wnt
smalt          2D PROCESSING
pp          9.2          sb1          -0.134
pp1v1          59          sbel          -0.099
presat          n          wfile1          ft
                                procl          4096
il          FLAGS          n
in          n          y
dp          2D ACQUISITION
hs          3608.8
sv1          256
phase          0
DISPLAY
sp          -17.3
wp          18082.5
vs          830
sc          25
wc          120
hmm          11.77
ls          500.00
rfl          26.1
rfd          0
ca          0
lms          100.000
al          2D DISPLAY
sp1          -16.0
wp1          3607.0
sc2          0
wc2          120
rfl1          17.7
rfd1          0

```

STANDARD 1H OBSERVE
 E187 B1-Benzylmethylester-MCP standard(08/03/2005)
 file name: E187B1
 Pulse Sequence: s2pul

Figure 4 ^1H NMR of **3b**.

^{13}C OBSERVE
 E187 B1-Benzylmethylester-MCP C13 standard(08/03/2005)
 file name: E187B1C13
 Pulse Sequence: s2pul

Figure 5 ^{13}C NMR of **3b**.


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HETCOR E387B1 H-C
in CDCl3 400 MHz
08/04/05
exp5 hetcor

SAMPLE
date Aug 4 2005 dfrq DEC. & VT 399.804
solvent CDCl3 dn H1
file /home/w2/het- dpr 37
COR-E387B1H-C.fid dof -212.4
ACQUISITION
sfreq 100.539 dms nmv
ta C13 dmf csw
at 0.150 dmq walz16
wz 5428 dres 90.0
sw 18091.4 hmc z
zb not used temp 30.0
hs 15 PROCESSING
ss 1 sb -0.022
tqwr 52 sbs 0.006
wv 8.4 wtfila
ql 1.000 proc ft
tof -300.0 fa 2048
nt 32 math f
ct 12
alock 0 werr cpreact('wait-
gain 60 7)
fsh 140.0 wexp procplot
fmb 0 wba
hmult n wat
dp 9.2 2D PROCESSING
pdv1 55 sb1 -0.066
presat flags n sb1a1 -0.060
il n prcl ft
in n prcl f1
gp y f1 1024
hs y
2D ACQUISITION
sw1 3609.8
ni 356
phase DISPLAY 0
sp -5.5
wp 18075.5
vs 2482
sc 25
wo 120
hmm 150.41
is 500.00
rfl 26.1
rfd 0
is 100.000
2D DISPLAY
sp1 -10.7
wp1 3609.8
sc2 0
wo2 120
rfl1 17.7
rfd1 0

```

```

HETCOR E387B1 H-C
in CDCl3 400 MHz
08/04/05
Data Collected on:
inova400-inova400
Archive directory:
Sample directory:
File: HETCOR-E387B1H-C
Pulse Sequence: hetcor
Solvent: CDCl3

```

Figure 6 ^1H - ^{13}C HETCOR NMR of **3b**.

STANDARD IN OBSERVE
 E387productC1 (08/18/2005)
 file name: E387Clagala
 Pulse Sequence: s2pul

Figure 9 ^1H NMR of 3d.

13C OBSERVE
 E387Cl C13- allylMCP standard spectra(08/03/2005)
 file name: E387ClC13
 Pulse Sequence: s2pul

Figure 10 ^{13}C NMR of 3d.

STANDARD IN OBSERVE
 E187 final11-PropylMCP standard(07/20/2005)
 file name: E187final11
 Pulse Sequence: s2pul

Figure 11 ^1H NMR of **3e**.

13C OBSERVE
 E187final11 C13-PropylMCP C13 standard(07/20/2005)
 file name: E187final11C13
 Pulse Sequence: s2pul

Figure 12 ^{13}C NMR of **3e**.

Figure 13 Accurate mass spectrum of **3a**

Figure 14 Accurate mass spectrum of **3b**

Figure 15 Accurate mass spectrum of **3c**

Figure 16 Accurate mass spectrum of **3d**

Figure 17 Accurate mass spectrum of **3e**

Figure 18 UV-visible spectrum of **3a**.

Figure 19 UV-visible spectrum of **3b**.

Figure 20 UV-visible spectrum of **3c**.

Figure 21 UV-visible spectrum of **3d**.

Figure 22 UV-visible spectrum of **3e**.

Figure 23 UN-visible spectrum of **Co-3a**.

Table S1. Crystal data and structure refinement for **3a**.

Identification code	3a	
Empirical formula	C ₄₈ H ₃₆ N ₄ O ₂	
Formula weight	700.81	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 10.4497(15) Å	α = 66.129(2)°.
	b = 12.7182(18) Å	β = 84.317(2)°.
	c = 15.180(2) Å	γ = 74.029(2)°.
Volume	1773.4(4) Å ³	
Z	2	
Density (calculated)	1.312 Mg/m ³	
Absorption coefficient	0.081 mm ⁻¹	
F(000)	736	
Crystal size	0.30 x 0.30 x 0.05 mm ³	
Theta range for data collection	1.47 to 25.00°.	
Index ranges	-12 ≤ h ≤ 12, -15 ≤ k ≤ 15, -18 ≤ l ≤ 18	
Reflections collected	12889	
Independent reflections	6195 [R(int) = 0.0231]	
Completeness to theta = 25.00°	99.4 %	
Absorption correction	Empirical SADABS	
Max. and min. transmission	0.9960 and 0.7763	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	6195 / 0 / 496	
Goodness-of-fit on F ²	1.098	
Final R indices [I > 2σ(I)]	R1 = 0.0565, wR2 = 0.1658	
R indices (all data)	R1 = 0.0733, wR2 = 0.1750	
Largest diff. peak and hole	0.726 and -0.264 e.Å ⁻³	

Table S2. Crystal data and structure refinement for **Co-3a**.

Identification code	Co-3a	
Empirical formula	C ₆₀ H ₅₅ Co N ₅ O ₂	
Formula weight	937.02	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 13.029(4) Å	$\alpha = 77.699(4)^\circ$.
	b = 13.734(4) Å	$\beta = 79.722(4)^\circ$.
	c = 13.913(4) Å	$\gamma = 67.390(4)^\circ$.
Volume	2232.5(10) Å ³	
Z	2	
Density (calculated)	1.319 Mg/m ³	
Absorption coefficient	0.431 mm ⁻¹	
F(000)	927	
Crystal size	0.15 x 0.07 x 0.05 mm ³	
Theta range for data collection	1.51 to 25.00°.	
Index ranges	-15 ≤ h ≤ 15, -16 ≤ k ≤ 15, -16 ≤ l ≤ 16	
Reflections collected	15880	
Independent reflections	7843 [R(int) = 0.0756]	
Completeness to theta = 25.00°	99.4 %	
Absorption correction	Empirical SADABS	
Max. and min. transmission	0.9788 and 0.4524	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	7843 / 0 / 551	
Goodness-of-fit on F ²	0.964	
Final R indices [I > 2σ(I)]	R1 = 0.0988, wR2 = 0.2454	
R indices (all data)	R1 = 0.1643, wR2 = 0.2793	
Largest diff. peak and hole	1.711 and -0.563 e.Å ⁻³	