Supporting Information for Ms. No:

Contracted and Expanded *Meso*-Alkynyl Porphyrinoids: from Triphyrin to Hexaphyrin

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Table of Contents of Supporting Information.

Page S1–S2	Procedures for synthesis of metal complexes ZnCl ₃ , Zn ₂ , Ni ₂ , Pt ₂ and Ni ₇ .
Page S3	Table S1. Summary of crystal data for Zn ₂ , Ni ₂ , Pt ₂ and H ₄ 6 (PhMe solvate).
Page S4	Figure S1. Solid state structures of Zn ₂ , Ni ₂ and Pt ₂ .
Page S5	Figure S2. ¹ H NMR spectrum of pentaphyrin H ₄ 5 .
Page S6	Figure S3. ¹³ C NMR spectrum of pentaphyrin H ₄ 5 .
Page S7	Figure S4. ¹ H NMR spectrum of corrole H ₃ 4 .
Page S8	Figure S5. ¹³ C NMR spectrum of corrole H ₃ 4 .
Page S9	Figure S6. ¹ H NMR spectrum of triphyrin H ₃ .
Page S10	Figure S7. ¹³ C NMR spectrum of triphyrin H ₃ .
Page S11	Figure S8. ¹ H NMR spectrum of tripyrrenone H ₄ 7 .
Page S12	Figure S9. ¹³ C NMR spectrum of tripyrrenone H ₄ 7 .

Procedures for Synthesis of Metal Complexes ZnCl₃, Zn₂, Ni₂, Pt₂ and Ni₇.

Zinc Porphyrin Zn₂: The free-base porphyrin was metallated with zinc in quantitative yield by treatment with excess Zn(OAc)₂·2H₂O in 1:1 methanol dichloromethane. UV/vis (CH₂Cl₂) λ_{max} , nm (log ϵ): 502 (5.47), 650 (4.15), 708 (4.17). ¹H NMR (250 MHz, CDCl₃): δ 4.13 (16H, q, J = 7.3 Hz) 1.66 (24H, t, J = 7.3 Hz), 1.30–1.36 (84H, m). ¹³C NMR (62.5 MHz, CDCl₃): δ 146.5, 145.7, 113.1, 106.9, 99.7, 20.9, 18.7, 17.9, 12.0. FAB-MS: m/z 1319.0 (M⁺). Anal. Calcd for C₈₀H₁₂₄N₄Si₄Zn: C, 72.81; H, 9.47; N, 4.25. Found C, 72.23; H, 9.61; N, 4.22.

Nickel(II) porphyrin Ni2: The free-base porphyrin **H₂2** (31.5 mg, 25 μ mol) was mixed with Ni(acac)₂ (100 mg, 389 μ mol) and phenol (200 mg) in a test tube. The mixture was refluxed for 5 min. The product was purified by flash chromatography (SiO₂/CH₂Cl₂). Yield: 30 mg, 92 %. λ_{max} (CH₂Cl₂)/nm (log ϵ): 505 (5.18), 638 (4.19), 690 (3.89); ¹H NMR (200 MHz, CDCl₃): δ_{H} 3.93 (16H, q, J = 7.2 Hz), 1.74 (24H, t, J = 7.2), 1.13–1.3 (84H, m); ¹³C NMR (50 MHz, CDCl₃): δ_{C} 148.5, 137.5, 116.3, 103.9, 97.8, 20.7, 18.7, 17.8, 11.8. FAB-MS: m/z 1310.5 (M⁺; C₈₀H₁₂₄N₄Si₄Ni requires 1310.8).

Platinum(II) porphyrin Pt2: The free-base porphyrin **H₂2** (30 mg, 24 μ mol) was mixed with PtCl₂ (30 mg, 113 μ mol) and benzonitrile (2 mL) in a test tube. The mixture was refluxed for 35 min. The product was purified by flash chromatography (SiO₂/CH₂Cl₂). Yield: 8.7 mg, 25 %. λ_{max} (CH₂Cl₂)/nm (log ϵ): 489 (5.09), 623 (4.06), 668 (3.86); ¹H NMR (250 MHz, CDCl₃): δ_{H} 4.07 (16H, q, J = 7.2 Hz), 1.76 (24H, t, J = 7.2 Hz), 1.20–1.33 (84H, m); ¹³C NMR (62.5 MHz, CDCl₃): δ_{C} 146.7, 136.6, 117.8, 104.2, 102.0, 21.0, 18.7, 18.0, 11.8; FAB-MS: m/z 1448.0 (M⁺; C₈₀H₁₂₄N₄Si₄Pt requires 1449.29).

Zinc Triphyrin ZnCl3: A solution of free-base triphyrin **H3** (110 mg, 96 μ mol) in dichloromethane (1 mL) was treated with a solution of zinc(II) chloride (0.5 mL, 1 M in Et₂O). After stirring for 30 min the product was purified by flash chromatography (SiO₂/CH₂Cl₂); yield 67 mg, 56 %. UV/vis (CH₂Cl₂) λ_{max} , nm (log ϵ): 348 (4.51), 476 (4.16), 598 (4.04), 728 (4.31). ¹H NMR (500 MHz, CDCl₃): δ 6.61 (1H, d, J = 2.0 Hz), 6.20 (1H, d, J = 2.0 Hz), 3.50–3.68 (4H, m), 3.14–3.20 (1H, m), 3.08–2.85 (5H, m), 2.75–2.70 (1H, m), 2.59–2.64 (1H, m), 1.35–0.97 (102H, m). ¹³C NMR (62.5 MHz, CDCl₃): δ 165.1, 162.5, 161.8, 161.1, 152.1, 151.3, 146.5, 146.3, 145.3, 144.6, 143.5, 142.2, 141.8, 139.9, 110.2, 106.8, 105.0, 104.8, 104.6, 103.5, 103.1, 102.8, 96.6, 95.9, 19.1, 19.0, 18.9, 18.86, 18.83, 18.75, 18.71, 18.68, 18.4, 17.7, 16.3, 16.1, 16.0, 15.8, 11.9, 11.8, 11.6. FAB-MS: m/z 1235.7 (M⁺, C₇₂H₁₁₅N₃Si₄ZnCl requires 1235.88).

Ni7: A mixture of free-base **H₂7** (18 mg, 18 μ mol) and nickel(II) chloride (20 mg, 154 μ mol) and chloroform (2 mL) was heated to reflux for 5 min. The product was purified by flash chromatography (SiO₂/CH₂Cl₂); yield 16 mg, 92 %. UV/vis (CH₂Cl₂) λ_{max} , nm (log ϵ): 366 (4.43), 407 (4.49), 688 (4.03), 742 (4.29). ¹H NMR (200 MHz, CDCl₃): δ 3.21 (2H, q, J = 7.5 Hz), 3.12 (2H, q, J = 7.5 Hz), 3.08–3.01 (4H, m), 2.85 (2H, q, J = 7.5 Hz), 2.38 (2H, q, J = 7.5 Hz), 1.27–1.10 (81H, m). ¹³C NMR (62.5 MHz, CDCl₃): δ 179.7, 165.1, 160.2, 159.8, 152.1, 150.8, 145.9, 144.4, 142.5, 139.5, 138.8, 138.5, 134.7, 110.8, 107.9, 104.4, 103.0, 102.9, 100.9, 100.8, 93.8, 20.1, 19.7, 18.8, 18.7, 18.6, 18.5, 18.3, 17.7, 17.4, 17.3, 16.7, 16.0, 15.9, 15.3, 14.1, 11.9, 11.7, 11.3. FAB-HRMS calcd for (C₆₀H₉₃N₃O₂Si₃Ni + H⁺) 1030.6007, found 1030.6044.

Table S1. Summary of crystal data for Zn**2**, Ni**2**, Pt**2** and H₄**6** (toluene solvate).

	Zn 2	Ni 2	Pt 2	H ₄ 6
formula	C ₈₀ H ₁₂₄ N ₄ Si ₄ Zn ·2CH ₄ O·0.5C ₇ H ₈	C ₈₀ H ₁₂₄ N ₄ Si ₄ Ni ·C ₂ H ₂ Cl ₄	C ₈₀ H ₁₂₄ N ₄ Si ₄ Pt ·CH ₂ Cl ₂ ·H ₂ O	C ₁₂₀ H ₁₉₀ N ₆ Si ₆ ·2C ₇ H ₈
formula weight	1429.75	1480.75	1552.23	2069.62
crystal system	triclinic	triclinic	triclinic	triclinic
space group	<i>P</i> −1	<i>P</i> −1	<i>P</i> −1	<i>P</i> −1
<i>a</i> /Å	15.4030(3)	15.4377(2)	15.2923(3)	18.0634(5)
<i>b</i> /Å	17.2992(4)	17.0745(2)	15.6848(4)	18.7545(5)
<i>c</i> /Å	18.1735(5)	18.5033(7)	18.9901(4)	19.4680(6)
α /°	77.4494(11)	77.8713(5)	107.0731(15)	86.4113(9)
β /°	87.2644(12)	89.7279(6)	106.1862(11)	88.034(1)
γ /°	65.4764(18)	63.8827(7)	93.165(1)	86.7733(13)
<i>V</i> /Å ³	4295.47(19)	4260.11(9)	4134.71(17)	6568.7(3)
<i>Z</i>	2	2	2	2
<i>T</i> /K	150	150	150	150
cryst size, mm ³	0.4 × 0.3 × 0.2	0.2 × 0.2 × 0.2	0.2 × 0.1 × 0.1	0.2 × 0.2 × 0.1
reflections measured	27653	35871	26417	18554
unique reflections	14986	19394	17821	18554
<i>R</i> ₁	0.0893	0.0494	0.0640	0.1163
<i>R</i> _{w2}	0.1037	0.0598	0.0728	0.1194

Crystallization Procedures: Zn**2** and H₄**6** were crystallized from toluene by layered addition of methanol; Ni**2** was crystallized from 1,1,2,2-tetrachloroethane by layered addition of methanol; Pt**2** was crystallized from dichloromethane by layered addition of methanol. Crystal data for Zn**2**, Ni**2**, Pt**2** and H₄**6** (toluene solvate) are summarized in Table S1. All these data were collected on a Enraf Nonius Kappa CCD diffractometer. The following software was used for crystallographic analysis: COLLECT for data collection; DENZO and SCALEPACK for cell refinement and data reduction; SIR92 and SIR97 for structure solution; CRYSTALS for refinement. All the structures were refined on *F*.

Figure S1. Solid state structures of Zn2, Ni2 and Pt2 (hydrogens omitted for clarity; 50% probability ellipsoids).

Figure S2. ^1H NMR spectrum of pentaphyrin **H₄5** (250 MHz, CDCl_3 ; peaks at 7.2 and 2.35 ppm are due to toluene).

Figure S3. ^{13}C NMR spectrum of pentaphyrin $\text{H}_4\mathbf{5}$ (62.5 MHz, CDCl_3 ; peaks at 137.8, 129.0, 128.2, 125.3, and 21.4 ppm are due to toluene).

Figure S4. ^1H NMR spectrum of corrole $\text{H}_3\text{4}$ (250 MHz, CDCl_3).

Figure S5. ^{13}C NMR spectrum of corrole $\text{H}_3\text{4}$ (62.5 MHz, CDCl_3).

Figure S7. ^{13}C NMR spectrum of triphyrin H3 (125 MHz, CDCl_3).

Figure S8. ^1H NMR spectrum of tripyrrenone $\text{H}_2\mathbf{7}$ (250 MHz, CDCl_3 ; peak at 5.295 is due to dichloromethane).

Figure S9. ^{13}C NMR spectrum of tripyrrenone $\text{H}_2\text{7}$ (62.5 MHz, CDCl_3 ; peak at 53.38 is due to dichloromethane).