Electronic Supplementary Information

Synthesis and dynamic structure of multinuclear Rh complexes of porphyrinoids
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1. Synthetic procedure and spectroscopic data for 2, 3, 4, 5, and 6,

Expanded rosarin 2 and expanded octaphyrin 3
A mixture of 1,4-bis(3,4-diethylpyrrol-2-yl)benzene 1 (151.3 mg, 0.472 mmol), benzaldehyde (78 μL, 0.764 mmol), and trifluoroacetic acid (10 μL, 0.131 mmol) in dry CH2Cl2 (30 mL) was stirred for 24 h under argon at room temperature. The color of the solution changed from thin yellow to blue. 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone (438.8 mg, 1.93 mmol) was added to the reaction mixture with color change from blue to purple and stirring was continued for 2 h at room temperature. The reaction mixture was passed through celite and the filtrate was combined with CH2Cl2 washings. The CH2Cl2 solution was washed with aqueous 10% NaOH solution (20 mL). The aqueous layer was extracted with CH2Cl2 (5 x 20 mL). The combined organic layer was washed with water, dried over anhydrous Na2SO4, and then evaporated to dryness. The residue was chromatographed on silica gel. A purple fraction eluted with diethyl ether – hexane (1:5) gave rosarin 2 in 61% yield after recrystallization from CH2Cl2 – hexane. A red fraction eluted with diethyl ether – hexane (1:3) gave octaphyrin 3 in 8% yield after recrystallization from CH2Cl2 – hexane.

2: 1H NMR (400MHz, CDCl3) 11.79 (br s, 1H, C-H), 7.80 (s, 4H, bridge C6-H4), 7.52 (m, 2H, meso-phenyl-o-H), 7.47 (m, 1H, meso-phenyl-p-H), 7.41 (m, 2H, meso-phenyl-m-H), 2.56 (q, J = 7.4 Hz, 2H, C6H2CH3), 1.67 (q, J = 7.4 Hz, 2H, CH2CH3), 1.07 (t, J = 7.5 Hz, 3H, CH2C3H7), 0.72 (t, J = 7.4 Hz, 3H, CH2C3H7): 13C-NMR (δ-value in CDCl3) 15.4, 16.7, 18.3, 19.6, 127.7(x2), 131.0, 133.1, 134.3, 138.4, 138.6, 140.4, 142.7, 152.3; UV/Vis (CH2Cl2): λmax (log ε) 318.5 (4.85), 503.5 (5.10) nm; MS (ESI in MeOH): m/z 1220.587 (calcd for C87H91N6 (M + H+): 1220.733). Anal. Calcd for C87H90N6·2H2O: C, 83.21; H, 7.55; N, 6.69 %. Found: C, 83.19; H, 7.69; N, 6.44 %.

3: 1H NMR (400MHz, CDCl3) 14.75 (br s, 1H, C-H), 7.70 (s, 4H, bridge C6-H4), 7.41 – 7.54 (m, 5H, meso-phenyl-H), 2.55 (q, J = 7.4 Hz, 2H, CH2CH3), 1.59 (q, J = 7.2 Hz, 2H, CH2CH3), 1.05 (t, J = 7.5 Hz, 3H, CH2CH3): 13C-NMR (δ-value in CDCl3) 15.4, 16.8, 18.0, 18.5, 127.6, 128.3, 130.0(x2), 131.7, 134.0, 137.8, 137.9, 138.5, 143.5, 151.0; UV/Vis
(CH₂Cl₂): \(I_{\text{max}} \text{(log } \epsilon \text{)} 331.0 \text{ (4.97), 420.5 \text{ (4.66), 546.5 \text{ (5.04) nm; MS (ESI in MeOH): } m/z 1626.924 \text{ (calcd for C}_{116}\text{H}_{121}\text{N}_8 (M + H⁺): 1626.974). Anal. Calcd for C}_{116}\text{H}_{120}\text{N}_8: C, 85.67; H, 7.44; N, 6.89 \text{%. Found: C, 85.48; H, 7.65; N; 6.61 \text{%.}

Tris(dicarbonylrhodium) complex 4
A mixture of rosarin 2 (18.1 mg, 0.0148 mmol), [Rh(CO)₂Cl]₂ (31.4 mg, 0.0808 mmol), and K₂CO₃ (143.2 mg, 1.04 mmol) in dry CH₂Cl₂ (5 mL) was stirred for 24 h under argon at room temperature. Solvent was removed under reduced pressure and the residue was chromatographed on alumina. A purple fraction eluted with toluene was collected and recrystallized from CH₂Cl₂ – hexane to give 4 in 88% yield. UV-Vis (\(I_{\text{max}} \text{ nm (log } \epsilon \text{)} \text{ in CH₂Cl₂) 436 (4.51), 556 (5.17), 640 (sh, 3.87). ¹H-NMR (\(d\) value in CD₂Cl₂) 8.14, 7.63 (s \(2, 6H \) \(2, \) phenylene-\(H\)); 7.55 ~ 7.39 (m, 15H, meso-Ph-\(H\)); 2.50, 2.25, 1.59, 1.41 (m \(4, 6H \) \(4, -\text{CH₂CH₃}\)); 0.71, 0.73 (t \(2, 18H \) \(2, J = 6.8, 7.1 \text{ Hz, } -\text{CH₂CH₃}\)). ¹³C-NMR (\(d\) value in CDCl₃) 14.9, 17.0, 18.4, 20.0, 127.1, 127.8, 128.4, 129.5, 129.7, 130.8, 131.5, 134.1, 135.1, 137.6, 138.6, 145.2, 147.1, 162.9, 184.2 (CO, J_{Rh-H} = 67.1 \text{ Hz}). IR (KBr) 2068, 1996 cm⁻¹ (\(\nu \text{(CO)}\)). ESI-MS (found/calcd for C₉₃H₈₇N₆O₆Rh₃) 1693.29/1693.39. Analysis calcd. for C₉₃H₈₇N₆O₆Rh₃·H₂O: C, 65.27; H, 5.24; N, 4.91. Found: C, 64.81; H, 5.33; N, 4.81.

Tetrakis(dicarbonylrhodium) complex 5
A mixture of octaphyrin 3 (15.0 mg, 0.0092 mmol), [Rh(CO)₂Cl]₂ (19.3 mg, 0.0497 mmol), and K₂CO₃ (88.1 mg, 0.64 mmol) in dry CH₂Cl₂ (5 mL) was stirred for 18 h under argon at room temperature. Solvent was removed under reduced pressure and the residue was chromatographed on alumina. A purple fraction eluted with toluene was collected and recrystallized from CH₂Cl₂ – hexane to give 4 in 87% yield. UV-Vis (\(I_{\text{max}} \text{ nm (log } \epsilon \text{)} \text{ in CH₂Cl₂) 423 (4.72), 571 (5.38), 652 (sh, 4.08). ¹H-NMR (\(d\) value in CD₂Cl₂) 8.08, 7.58 (s \(2, 8H \) \(2, \) phenylene-\(H\)); 7.59, 7.39 (d \(2, 4H \) \(2, \) meso-Ph-\(o-H\)); 7.51 ~ 7.44 (m, 12H, meso-Ph-\(m,p-H\)); 2.51, 2.28, 1.63, 1.43 (m \(4, 8H \) \(4, -\text{CH₂CH₃}\)); 0.91, 0.72 (t \(2, 24H \) \(2, J = 7.4 \text{ Hz, } -\text{CH₂CH₃}\)). ¹³C-NMR (\(d\) value in CDCl₃) 15.4, 17.0, 17.9, 19.8, 127.1, 127.7, 128.3, 128.7, 129.6, 130.8, 132.5, 132.6, 135.2, 138.5, 138.6, 144.8, 146.8, 163.2, 183.5 (CO, J_{Rh-H} = 67.5 \text{ Hz}). IR (KBr) 2060, 1992 cm⁻¹ (\(\nu \text{(CO)}\)). ESI-MS (found/calcd for C₁₂₄H₁₁₆N₈O₈Rh₄) 2257.72/2257.52. Analysis calcd. for C₁₂₄H₁₁₆N₈O₈Rh₄·H₂O: C, 65.27; H, 5.23; N, 4.92. Found: C, 65.10; H, 5.21; N, 4.98.

Dicarbonylrhodium complex 6
A mixture of rosarin 2 (21.7 mg, 0.0178 mmol) and [Rh(CO)₂Cl]₂ (7.5 mg, 0.0193 mmol) in dry CH₂Cl₂ (10 mL) was stirred for 3 h under argon at room temperature. Solvent was removed under reduced
pressure and the residue was chromatographed on alumina. A purple fraction eluted with diethyl ether was collected. It was further chromatographed on silica gel and a red fraction eluted with diethyl ether – hexane (3:1) was collected. Solvent was removed and the residue was recrystallized from diethyl ether – methanol to give 6 in 31% yield. UV-Vis ($\lambda_{\text{max}}$ nm ($\log\epsilon$) in CH$_2$Cl$_2$) 521 (4.93), 541 (sh, 4.90), 622 (sh, 4.22). $^1$H-NMR ([δ value in CDCl$_3$]) 11.00 (br, 2H, NH); 8.04, 7.95 (d $\delta$ 2, 4H $\delta$ 2, $J = 8.1$, 7.9 Hz, phenylene-H); 7.95 (s, 4H, phenylene-H); 7.58 ~ 7.38 (m, 15H, meso-Ph-H); 2.70, 2.62, 2.43, 1.73, 1.71, 1.56 (q $\delta$ 6, 4H $\delta$ 6, $J = 7.4$, 7.8 Hz, -CH$_2$CH$_3$); 1.19, 1.11, 0.83, 0.75, 0.73, 0.71 (t $\delta$ 6, 6H $\delta$ 6, $J = 7.4$ Hz, -CH$_2$CH$_3$). IR (KBr) 2064, 1992 cm$^{-1}$ ($\nu$(CO)). ESI-MS (found/calcd for C$_{89}$H$_{89}$N$_6$O$_2$Rh + nH$^+$) 1378.61/1378.62 (n=1); 689.82/689.81 (n=2). Analysis calcd. for C$_{89}$H$_{89}$N$_6$O$_2$Rh·H$_2$O: C, 76.59; H, 6.57; N, 6.02. Found: C, 76.10; H, 6.87; N, 5.61.

**Figure 1.** $^1$H NMR spectra of the [Rh(CO)$_3$] complex 4 (bottom) and the Rh(CO)$_2$ complex 6 (top) in CDCl$_3$ at room temperature.
**Figure 2.** Variable temperature $^1$H NMR spectra of the Rh(CO)$_2$ complex 6 in toluene-$d_8$ at 20, 0, -20, -40, -60 °C.
Figure 3. \(^1\)H NMR ROESY spectrum of the \([\text{Rh(CO)}_2]_3\) complex 4 in toluene-\(d_8\) at 20 °C measured at mixing time 0.2 sec. The cross peaks between 7.6 and 8.3 ppm indicates that the 1,4-phenylene protons at the inside position and the outside position in the \(C_3\) isomer are exchanging.