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 μ L, 0.764 mmol), and trifluoroacetic acid (10 μ L, 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 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.

2: ¹H NMR (δ , 400MHz, CDCl₃) 11.79 (br s, 1H × 3, N*H*), 7.80 (s, 4H × 3, bridge C₆*H*₄), 7.52 (m, 2H × 3, *meso*-phenyl-*o*-*H*), 7.47 (m, 1H × 3, *meso*-phenyl-*p*-*H*), 7.41 (m, 2H × 3, *meso*-phenyl-*m*-*H*), 2.56 (q, *J* = 7.4 Hz, 2H × 6, C*H*₂CH₃), 1.67 (q, *J* = 7.4 Hz, 2H × 6, C*H*₂CH₃), 1.07 (t, *J* = 7.5 Hz, 3H × 6, CH₂C*H*₃), 0.72 (t, *J* = 7.4 Hz, 3H × 6, CH₂C*H*₃); ¹³C-NMR (δ -value in CDCl₃) 15.4, 16.7, 18.3, 18.6, 127.7(x2), 128.9, 131.0, 133.1, 134.3, 138.4, 138.6, 140.4, 142.7, 152.3; UV/Vis (CH₂Cl₂): λ_{max} (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 (δ , 400MHz, CDCl₃) 14.75 (br s, 1H × 4, N*H*), 7.70 (s, 4H × 4, bridge C₆*H*₄), 7.41 – 7.54 (m, 5H × 4, *meso*-phenyl-*H*), 2.55 (q, *J* = 7.4 Hz, 2H × 8, C*H*₂CH₃), 1.59 (q, *J* = 7.2 Hz, 2H × 8, C*H*₂CH₃), 1.05 (t, *J* = 7.5 Hz, 3H × 8, CH₂C*H*₃), 0.69 (t, *J* = 7.4 Hz, 3H × 8, CH₂C*H*₃); 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): λ_{max} (log ε) 331.0 (4.97), 420.5 (4.66), 546.5 (5.04) nm; MS (ESI in MeOH): m/z 1626.924 (calcd for C₁₁₆H₁₂₁N₈ (M + H⁺): 1626.974). Anal. Calcd for C₁₁₆H₁₂₀N₈: C, 85.67; H, 7.44; N, 6.89 %. Found: C, 85.48; H, 7.65; N; 6.61 %.

Tris(dicarbonylrhodium) complex 4

A mixture of rosarin **2** (18.1 mg, 0.0148 mmol), $[Rh(CO)_2CI]_2$ (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 (λ_{max} nm (log_E) in CH₂Cl₂) 436 (4.51), 556 (5.17), 640 (sh, 3.87). ¹H-NMR (δ -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, -CH₂CH₃); 0.71, 0.73 (t × 2, 18H × 2, *J* = 6.8, 7.1 Hz, -CH₂CH₃). ¹³C-NMR (δ -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 Hz). IR (KBr) 2068, 1996 cm⁻¹ (v(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), $[Rh(CO)_2CI]_2$ (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 (λ_{max} nm (log ϵ) in CH₂Cl₂) 423 (4.72), 571 (5.38), 652 (sh, 4.08). ¹H-NMR (δ -value in CDCl₃) 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, -CH₂CH₃); 0.91, 0.72 (t × 2, 24H × 2, *J* = 7.4 Hz, -CH₂CH₃). ¹³C-NMR (δ -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 Hz). IR (KBr) 2060, 1992 cm⁻¹ (v(CO)). ESI-MS (found/calcd for C₁₂₄H₁₁₆N₈O₈Rh₄) 2257.72/2257.52. Analysis calcd. for C₁₂₄H₁₁₆N₈O₈Rh₄·H₂O: C, 65.44; 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 CH_2Cl_2 (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 (λ_{max} nm (log ϵ) in CH₂Cl₂) 521 (4.93), 541 (sh, 4.90), 622 (sh, 4.22). ¹H-NMR (δ -value in CDCl₃) 11.00 (br, 2H, N*H*); 8.04, 7.95 (d × 2, 4H × 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 × 6, 4H × 6, *J* = 7.4, 7.8 Hz, -CH₂CH₃); 1.19, 1.11, 0.83, 0.75, 0.73, 0.71 (t × 6, 6H × 6, *J* = 7.4 Hz, -CH₂CH₃). IR (KBr) 2064, 1992 cm⁻¹ (v(CO)). ESI-MS (found/calcd for C₈₉H₈₉N₆O₂Rh + nH⁺) 1378.61/1378.62 (n=1); 689.82/689.81 (n=2). Analysis calcd. for C₈₉H₈₉N₆O₂Rh·H₂O: C, 76.59; H, 6.57; N, 6.02. Found: C, 76.10; H, 6.87; N, 5.61.

Figure 1. ¹H NMR spectra of the $[Rh(CO)_2]_3$ complex 4 (bottom) and the $Rh(CO)_2$ complex 6 (top) in CDCl₃ at room temperature.



20 °C 0 °C -20 °C WW -40 °C 14 M -60 °C 7 6 0 ppm 8 1 3 1 13 12 11 9 2

Figure 2. Variable temperature ¹H NMR spectra of the Rh(CO)₂ complex **6** in toluene- d_8 at 20, 0, -20, -40, -60 °C.

Figure 3. ¹H NMR ROESY spectrum of the $[Rh(CO)_2]_3$ 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_{3v} isomer are exchanging.

