

Supplementary Information for

Dithiaethyneazuliporphyrin – A Contracted Heterocarbaporphyrin

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Experimental details and spectral data of **2** and **4**

Dithiaethyneazuliporphyrin (S₂EATPP)H (**2**):

Azulene (44 mg, 0.34 mmol), 1,4-bis(5-(phenylhydroxymethyl)thien-2-yl)-1,4-diphenyl-2-butyne **3** (0.2 g, 0.34 mmol) and freshly distilled CH₂Cl₂ (150 mL) were placed in a 500-mL flask. Nitrogen was bubbled through the solution for 20 min, then Et₂O:BF₃ (40 μL, 0.3 mmol) was added and the mixture was stirred in the dark for 1 h under nitrogen. Triethylamine (84 μL, 0.6 mmol) and DDQ (0.54 g, 2.4 mmol) were added and the solution was stirred for 20 min. The solvent was evaporated to dryness. The residue was dissolved in dichloromethane and chromatographed on basic alumina. The first orange-brown fraction was eluted with dichloromethane and subjected to a second chromatography on basic alumina with benzene as an eluant. Recrystallization from CH₂Cl₂/CH₃OH produced **2** (35 mg, 15.4%).

UV-Vis (CHCl₃): λ_{max} (logε) = 402 (4.3), 436 (4.4), 490 (4.5), 515 (4.4), 629 nm (3.7); ¹H NMR (500 MHz, benzene-*d*₆, 298 K, TMS): δ = 8.14 (d, ³J(H,H) = 7.8 Hz, 4H; 3,18-*o*-Ph); 8.00, 7.91 (AB, ³J(H,H) = 5.5 Hz, 4H; 5,16-H, 6,15-H); 7.79 (m, 6H; 10¹,11¹-H, 8,13-*o*-Ph); 7.33 (t, ³J(H,H) = 7.3 Hz, 8H; *m*-Ph); 7.24 (t, ³J(H,H) = 7.3 Hz, 2H; 8,13-*p*-Ph); 7.18 (2H, 3,18-*p*-Ph); 6.55 (t, ³J(H,H) = 9.6 Hz, 1H; 10³-H); 6.23 (t, ³J(H,H) = 10.1 Hz, 2H; 10²,11²-H); 5.57 ppm (s, 1H; 20-H); ¹³C NMR (125.77 MHz, benzene-*d*₆, 298 K): δ = 152.3 (7,14-C), 145.3 (4,17-C), 141.3 (8,13-*i*-Ph), 139.0 (10³-C), 138.6 (3,18-*i*-Ph), 136.7 (10¹,11¹-C), 132.8 (6,15-C), 132.2 (5,16-C), 131.7 (8,13-*o*-Ph), 131.4 (10,11-C), 129.6 (3,18-*o*-Ph), 129.4 (9,12-C), 128.9 (3,18-*m*-Ph), 128.5 (8,13-*m*-Ph), 127.2 (8,13-*p*-Ph), 126.8 (3,18-*p*-Ph, 8,13-C), 126.5 (10²,11²-C), 120.2 (20-C), 112.0 (3,18-C), 106.1 ppm (1,2-C); HR-MS (ESI, *m/z*): 670.1790 (670.1789 calculated for [C₄₈H₃₀S₂]⁺).

Ruthenium(II) dithiaethyneazuliporphyrin (S₂EATPP)Ru^{II}(CO)₂Cl (**4**):

15 mg of **2** (0.022 mmol) and 1.1 g of Ru₃(CO)₁₂ (1.76 mmol) in 20 mL of freshly distilled chlorobenzene were refluxed for 4 h under nitrogen. The solvent was evaporated to dryness and the residue was chromatographed on silica gel. After an initial orange-red fraction was eluted with benzene, the second brown-green fraction eluted with dichloromethane was

collected and identified as **4**. The second chromatography on silica gel with dichloromethane as eluant and recrystallization from CHCl₃/hexane gave **4** in 5.5% yield (1 mg).

UV-Vis (CHCl₃): λ_{\max} = 373, 474, 508, 644, 693 nm; ¹H NMR (500 MHz, CD₂Cl₂, 220 K, TMS): δ = 8.53, 8.50 (AB, ³*J*(H,H) = 5.5 Hz, 4H; 5,16-H, 6,15-H); 8.36 (d, ³*J*(H,H) = 7.3 Hz, 2H; 8,13-*o*-Ph); 8.02 (d, ³*J*(H,H) = 7.3 Hz, 4H; 3,18-*o*-Ph); 7.87 (t, ³*J*(H,H) = 7.3 Hz, 2H; 8,13-*m*-Ph); 7.74 – 7.64 (m, 8H; 10¹,11¹-H, 3,18-*m*-Ph, 8,13-*p*-Ph); 7.62 – 7.48 (m, 7H; 10³-H, 3,18-*p*-Ph, 8,13-*o,m*-Ph); 7.15 ppm (t, ³*J*(H,H) = 9.6 Hz, 2H; 10²,11²-H); MS (ESI, *m/z*): 827.5 (827.0 calculated for [C₅₀H₂₉O₂S₂Ru]⁺).