

## B920676K ESI

### Experimental Part

**General.** All commercially available reagents were purchased and used without further purification.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded on Bruker spectrometers. UV-Vis absorption spectra were collected at room temperature on a UVIKON XL spectrometer from BIO-TEK instruments. Infrared spectra were measured either in KBr pellet using *Perkin Elmer* FTIR 1600 spectrometer or on a *Shimadzu* FTIR-8400S equipped with a *Pike* Miracle ATR (Ge).

The silica used for chromatography and atropoisomerisation was Geduran, Silica Gel Si60 (40-63  $\mu\text{m}$ ) from Merck. The aluminium oxide used for chromatography was Aluminium Oxide 90 standardized, from Merck.

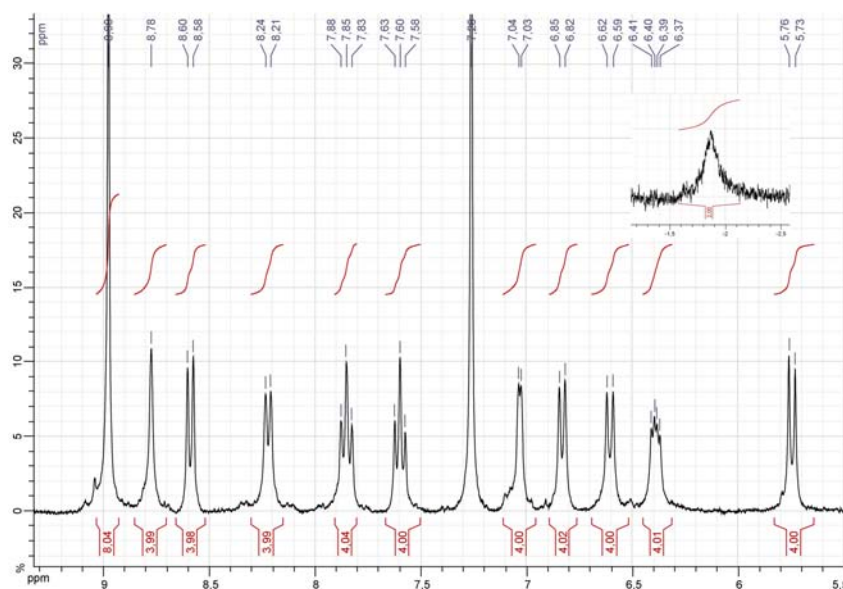
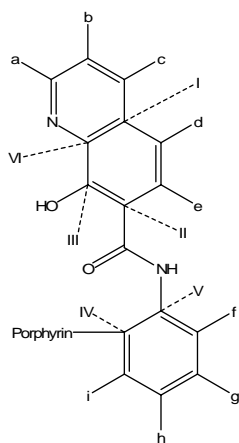
The 7-carboxy-8-hydroxyquinoline<sup>1</sup>, *meso*-tetrakis(o-aminophenyl)porphyrin<sup>2</sup> and  $\alpha_4$ -*meso*-tetrakis(o-aminophenyl)porphyrin (**1**)<sup>3</sup> were synthesised as described in literature.

### Porphyrin (2)

7-carboxy-8-hydroxyquinoline (495 mg, 2.6 mmol, 6 eq), compound **1** (295 mg, 0.44 mmol, 1 eq) and DMAP (*para*N,N-dimethylaminopyridine) (323 mg, 2.6 mmol, 6 eq) are dissolved in  $\text{CH}_2\text{Cl}_2$  (45 mL). HBTU (989 mg, 2.6 mmol, 6 eq) is added to the solution, the mixture is protected from light and stirred at room temperature under argon for 4 days. Half of the solvent is evaporated under reduced pressure, methanol (120 mL) is added and the mixture is stirred overnight. After centrifugation, the solid is filtered, washed with methanol and diethyl ether affording 469 mg of the desired porphyrin **2** as a purple solid (0.35 mmol, 80 % yield).

$^1\text{H-NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm): -1.87 (2H, br s,  $\text{NH}_{\text{porphyrin}}$ ), 5.75 (4H, d,  $J = 8.9$  Hz,  $\text{H}_d$ ), 6.39 (4H, dd,  $J = 7.9$  Hz and 3.9 Hz,  $\text{H}_b$ ), 6.61 (4H, d,  $J = 8.9$  Hz,  $\text{H}_e$ ), 6.83 (4H, d,  $J = 7.9$  Hz,  $\text{H}_c$ ), 7.03 (4H, d,  $J = 3.9$  Hz,  $\text{H}_a$ ), 7.60 (4H, dd,  $J = 7.4$  Hz and 7.4 Hz,  $\text{H}_h$ ), 7.85 (4H, dd,  $J = 7.4$  Hz and 7.4 Hz,  $\text{H}_g$ ), 8.22 (4H, d,  $J = 7.4$  Hz,  $\text{H}_f$ ), 8.59 (4H, d,  $J = 7.4$  Hz,  $\text{H}_i$ ), 8.78 (4H, br s,  $\text{NH}_{\text{amide}}$ ) and 8.98 (8H, s,  $\text{H}_{\beta\text{pyrr}}$ );  $^{13}\text{C-NMR}$  (HMBC-HSQC,  $\text{CDCl}_3$ )  $\delta$  (ppm): 111.4 ( $\text{C}_{\text{III}}$ ), 115.7 ( $\text{CH}_d$ ), 114.6 ( $\text{C}_{\text{VI}}$ ), 121.9 ( $\text{CH}_b$ ), 122.2 ( $\text{CH}_f$ ), 123.2 ( $\text{CH}_h$ ), 124.9 ( $\text{CH}_e$ ), 127.4 ( $\text{C}_I$ ), 129.8 ( $\text{CH}_g$ ), 131.6 ( $\text{CH}_{\beta\text{pyrr}}$ ), 133.4 ( $\text{CH}_i$ ), 133.9 ( $\text{CH}_c$ ), 134.9 ( $\text{C}_{\text{IV}}$ ), 138.8 ( $\text{C}_V$ ), 147.0 ( $\text{CH}_a$ ), 148.9 ( $\text{C}_{\text{II}}$ ) and 162.7 (CO).  $\lambda_{\text{max}}$  (nm) ( $\epsilon \times 10^{-4}/\text{L mol}^{-1} \text{cm}^{-1}$ ) ( $\text{CH}_2\text{Cl}_2$ ): 270 (7.7), 423 (28.8), 516 (1.7), 548 (0.4), 589 (0.6) and 645 (0.1).  $\nu_{\text{max}}(\text{KBr})/\text{cm}^{-1}$ : 3300, 1666, 1581, 1536, 1449, 1383, 1286, 1229, 1127 and 967.  $m/z$  (MALDI) 1359.45 ( $\text{MH}^+$ ).  $\text{C}_{84}\text{H}_{55}\text{N}_{12}\text{O}_8$

requires: 1359.43). (Found: C 70.2; H 3.9; N 11.7,  $C_{84}H_{54}N_{12}O_8 + CH_2Cl_2 + CH_3OH$  requires C 70.0; H 4.1; N 11.4)



### Complex: [2-Nd]<sup>+</sup>

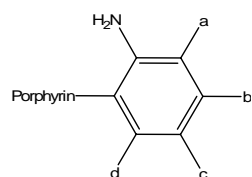
Porphyrin **2** (30.0 mg, 22  $\mu$ mol, 1 eq) is dissolved in analytical grade  $CH_2Cl_2$  (25 mL). A solution (22  $\mu$ L) of TBAOH (1M) in MeOH (22  $\mu$ mol, 1 eq) is added and the mixture is degassed during 10 minutes and then heated to reflux under argon. A solution of  $CH_2Cl_2$  (5 mL) containing  $Nd(acac)_3(H_2O)_2$  (10.5 mg, 22  $\mu$ mol, 1 eq) is added drop wise. The reaction mixture is refluxed under argon during 7 h.  $Et_2O$  (70 mL) is added and the precipitated solid is recovered by centrifugation and washed with  $Et_2O$ . The solid is dried under vacuum to yield 31.6 mg (18.1  $\mu$ mol, 82%) of a purple solid.

$\lambda_{max}$  (nm) ( $\epsilon \times 10^{-4}/L mol^{-1} cm^{-1}$ ) ( $CH_2Cl_2$ ): 270 (6.9), 427 (17.0), 520 (1.3), 565 (0.7), 591 (0.7) and 652 (0.2).  $\nu_{max}(KBr)/cm^{-1}$  2959, 2874, 1636, 1631, 1596, 1578, 1501, 1447, 1398,

1302, 1227, 1187, 1110, 982, 968, 883, 824, 797, 752 and 744.  $m/z$  (ESI<sup>-</sup>) 1496.24 (M<sup>-</sup>. C<sub>84</sub>H<sub>40</sub>N<sub>12</sub>O<sub>8</sub>Nd requires: 1496.30)

### Porphyrin 1-Pd

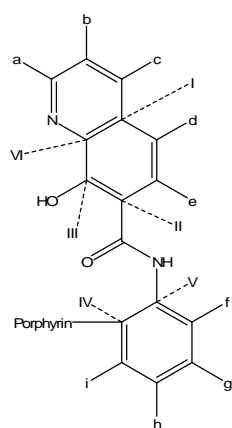
The metallation of the porphyrin has been performed using the general procedure.<sup>4</sup> A solution of the *meso*-tetrakis(*o*-aminophenyl)porphyrin<sup>2</sup> (100 mg, 0.15 mmol, 1 eq, mixture of atropoisomers) and of Pd(OAc)<sub>2</sub> (50 mg, 0.22 mmol, 1.5 eq) in a mixture of CHCl<sub>3</sub>/MeOH (2/1, 15 mL) is refluxed during 9 h under argon and protected from light. The reaction mixture is filtered on a silica pad and the solvents are removed under reduced pressure. The orange residue is dissolved in toluene (60 mL) and 5 g of silica gel is added. The mixture is heated to reflux under argon and protected from light for 20 h. The toluene is filtered off and the silica is washed with 150 mL of CH<sub>2</sub>Cl<sub>2</sub>-MeOH (95-5). The solvents are evaporated at room temperature under reduced pressure and the residue is loaded on an aluminium oxide chromatography column and eluted with a mixture of CH<sub>2</sub>Cl<sub>2</sub>-MeOH (98:2). Pure  $\alpha_4$  atropoisomer is obtained as an orange solid: 40 mg (0.05 mmol, 24%).



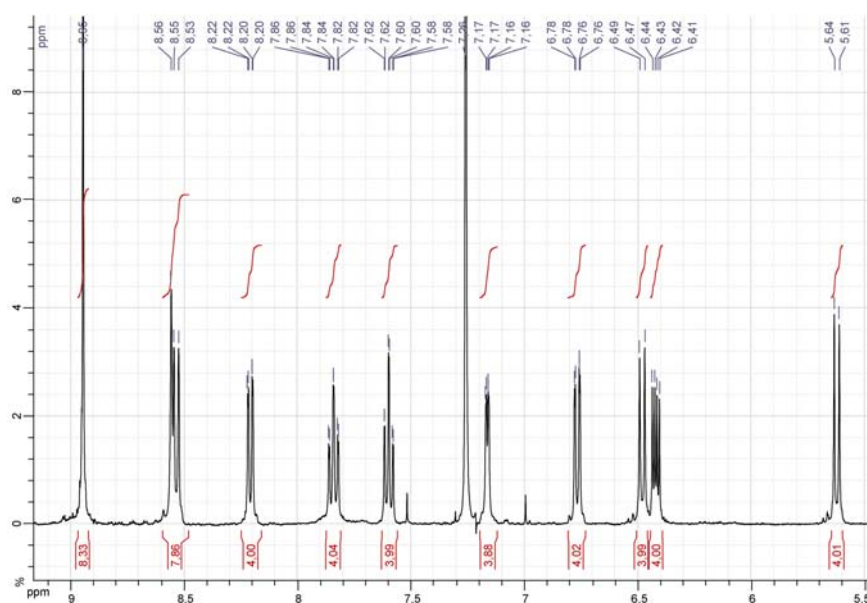
<sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm): 3.5 (8H, br s, NH<sub>2</sub>), 7.04 (4H, dd,  $J$  = 7.6 Hz and 1.0 Hz, H<sub>a</sub>), 7.13 (4H, ddd,  $J$  = 7.6 Hz, 7.6 Hz and 1.0 Hz, H<sub>c</sub>), 7.56 (4H, ddd,  $J$  = 7.6 Hz, 7.6 Hz and 1.0 Hz, H<sub>b</sub>), 7.79 (4H, dd,  $J$  = 7.6 Hz and 1.0 Hz, H<sub>c</sub>) and 8.86 (8H, s, H <sub>$\beta$</sub> -pyrr), <sup>13</sup>C-NMR (90 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm): 115.3 (CH), 117.5 (C), 117.7 (CH), 126.6 (C), 129.7 (CH), 131.3 (CH), 134.6 (CH), 141.9 (C) and 146.6 (C)

### Porphyrin 2-Pd

78 mg of 7-carboxy-8-hydroxyquinoline (0.41 mmol, 8 eq), 40 mg of **1-Pd** (0.05 mmol, 1 eq) and 50 mg of DMAP (0.41 mmol, 8 eq) are dissolved in 10 mL of analytical grade CH<sub>2</sub>Cl<sub>2</sub> and degassed. 156 mg of HBTU (0.16 mmol, 8 eq) are added to the solution, the mixture is protected from light and stirred at room temperature under argon for 5 days. Half of the CH<sub>2</sub>Cl<sub>2</sub> is evaporated under reduced pressure and 50 mL of methanol are added. The mixture is centrifugated and the solid is washed with 2 x 30 mL MeOH and dried with diethylether. 49 mg of an orange solid is obtained (0.03 mmol, 67%).



$^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm): 5.62 (4H, d,  $J = 8.8$  Hz,  $\text{H}_d$ ), 6.42 (4H, dd,  $J = 8.2$  Hz and 4.1 Hz,  $\text{H}_b$ ), 6.48 (4H, d,  $J = 8.8$  Hz,  $\text{H}_c$ ), 6.77 (4H, dd,  $J = 8.2$  Hz and 1.4 Hz,  $\text{H}_c$ ), 7.17 (4H, dd,  $J = 4.1$  Hz and 1.4 Hz,  $\text{H}_a$ ), 7.60 (4H, ddd,  $J = 7.6$  Hz, 7.6 Hz and 1.0 Hz,  $\text{H}_h$ ), 7.84 (4H, ddd,  $J = 7.8$  Hz, 7.8 Hz and 1.0 Hz,  $\text{H}_g$ ), 8.21 (4H, dd,  $J = 7.6$  Hz and 1.0 Hz,  $\text{H}_i$ ), 8.54 (4H, d,  $J = 7.6$  Hz,  $\text{H}_f$ ), 8.56 (4H, br s,  $\text{NH}_{\text{amide}}$ ) and 8.95 (8H, s,  $\text{H}_{\beta\text{pyrr}}$ );  $^{13}\text{C-NMR}$  (HSQC HMBC,  $\text{CDCl}_3$ )  $\delta$  (ppm): 111.4 ( $\text{C}_{\text{III}}$ ), 115.7 ( $\text{CH}_d$ ), 116.7 ( $\text{C}_{\text{VI}}$ ), 121.9 ( $\text{CH}_b$ ), 122.2 ( $\text{CH}_f$ ), 123.2 ( $\text{CH}_h$ ), 124.9 ( $\text{CH}_e$ ), 127.4 ( $\text{C}_i$ ), 129.8 ( $\text{CH}_g$ ), 131.6 ( $\text{CH}_{\beta\text{pyrr}}$ ), 133.4 ( $\text{CH}_i$ ), 133.9 ( $\text{CH}_c$ ), 134.9 ( $\text{C}_{\text{IV}}$ ), 138.8 ( $\text{C}_v$ ), 141.4 ( $\text{C}_{\text{Porph}}$ ), 147.0 ( $\text{CH}_a$ ), 148.9 ( $\text{C}_{\text{II}}$ ) and 162.7 (CO).  $\lambda_{\text{max}}$  (nm) ( $\epsilon \times 10^{-4}/\text{L mol}^{-1} \text{cm}^{-1}$ ) ( $\text{CH}_2\text{Cl}_2$ ): 274 (5.7), 421 (24.1), 527 (2.2) and 559 (0.5).  $\nu_{\text{max}}(\text{KBr})/\text{cm}^{-1}$  3300, 1666, 1581, 1536, 1461, 1441, 1383, 1350, 1309, 1281, 1229, 1195, 1127, 1102, 1072, 1014 and 939.  $m/z$  ( $\text{ESI}^+$ ) 1485.3110 ( $\text{MNa}^+ \text{C}_{84}\text{H}_{52}\text{N}_{12}\text{O}_8\text{PdNa}^+$  requires: 1485.2983).



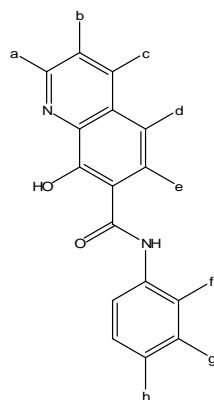
### Complex [(2-Pd)Nd]<sup>-</sup>

16.3 mg (11.1  $\mu\text{mol}$ , 1 eq) of porphyrin **2-Pd** in 17 mL  $\text{CH}_2\text{Cl}_2\text{-CH}_3\text{CN}$  (8-2) are degassed. 11  $\mu\text{L}$  of 1M TBAOH solution in MeOH (11  $\mu\text{mol}$ , 1 eq) are added and the mixture is heated to reflux under argon. 5.3 mg (11.1  $\mu\text{mol}$ , 1 eq) of neat  $\text{Nd}(\text{acac})_3(\text{H}_2\text{O})_2$  are added. The reaction mixture is refluxed under argon during 7 h. The desired product is precipitated with 60mL  $\text{Et}_2\text{O}$ , washed with  $\text{Et}_2\text{O}$  and dried under vacuum: 11.3 mg (6.1  $\mu\text{mol}$ , 55%) of a orange solid is isolated.

$\lambda_{\text{max}}$  (nm) ( $\epsilon \times 10^{-4}/\text{L mol}^{-1} \text{cm}^{-1}$ ) ( $\text{CH}_2\text{Cl}_2$ ): 278 (9.5), 424 (17.6), 529 (2.1) and 561 (0.7).  $\nu_{\text{max}}(\text{KBr})/\text{cm}^{-1}$  2960, 1635, 1500, 1447, 1397, 1354, 1306, 1233, 1191, 1102, 1013, 825, 794 and 749.  $m/z$  (ESI) 1600.1968 (M $^+$ .  $\text{C}_{84}\text{H}_{48}\text{N}_{12}\text{O}_8\text{PdNd}$  requires: 1600.1825)

### 7-(phenylcarboxamide)-8-hydroxyquinoline (3)

In a flask under argon and protected from light: 100 mg of 7-carboxy-8-hydroxyquinoline (0.53 mmol, 1 eq), 65 mg of DMAP (0.53 mmol, 1 eq), 48  $\mu\text{L}$  of aniline (0.53mmol, 1 eq) and 200 mg of HBTU (0.53 mmol, 1 eq) in 20 mL of analytical grade  $\text{CH}_2\text{Cl}_2$  are stirred at room temperature during 3 days. The solvent is evaporated under reduced pressure and the residue is washed with 20 mL MeOH and dried in air. 130 mg of an orange solid is obtained (0.49 mmol, 93%).



$^1\text{H-NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm): 7.16 (1H, tt,  $J = 7.6$  Hz and 1.2 Hz,  $\text{H}_h$ ), 7.36-7.42 (2H, m,  $\text{H}_g$ ), 7.45 (1H, d,  $J = 8.9$  Hz,  $\text{H}_d$ ), 7.57 (1H, dd,  $J = 8.5$  Hz and 4.2 Hz,  $\text{H}_b$ ), 7.75-7.79(2H, m,  $\text{H}_f$ ), 8.22 (1H, dd,  $J = 8.5$  Hz and 1.6 Hz,  $\text{H}_c$ ), 8.31 (1H, d,  $J = 8.8$  Hz,  $\text{H}_e$ ), 8.86 (1H, dd,  $J = 4.2$  Hz and 1.6 Hz,  $\text{H}_a$ ) and 9.90 (1H, br s,  $\text{NH}_{\text{amide}}$ ).  $^1\text{H-NMR}$  (90 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm): 118.0 (CH), 120.5(CH), 123.5(CH), 124.3(CH), 127.9(CH), 129.1(CH), 130.1(C), 136.4(CH), 138.2'(C), 138.4(C), 148.4(CH), 151.0(C) and 163.3(C).  $\lambda_{\text{max}}$  (nm) ( $\epsilon \times 10^{-4}/\text{L mol}^{-1} \text{cm}^{-1}$ ) ( $\text{CH}_2\text{Cl}_2$ ): 271 (18000).  $\nu_{\text{max}}(\text{ATR})/\text{cm}^{-1}$  3019, 1657, 1692, 1551, 1525, 1500, 1471, 1445, 1423, 1377, 1334, 1285, 1232, 1213, 1183, 1175, 1124, 1109, 1077, 1039, 1016, 943,

889, 824, 810, 754, 735, 689, 651 and 607. (Found: C 71.64; H 4.55; N 10.56,  $C_{16}H_{12}N_2O_2 + 0.25 H_2O$  requires C 71.52; H 4.70; N 10.42)

### Complex [(3)<sub>4</sub>Nd]

40.0 mg (151  $\mu$ mol, 4 eq) of **3**, and 18.0 mg (37.8  $\mu$ mol, 1 eq)  $Nd(acac)_3$  are dissolved in 30 mL of a  $CH_2Cl_2$ - $CH_3CN$  mixture (8-2). 37.8  $\mu$ L of 1M TBAOH solution in MeOH (37.8  $\mu$ mol, 1 eq) is added. The mixture is stirred at room temperature for 1 day and concentrated to 5 mL. 40 mL  $Et_2O$  are added and the yellow precipitate is recovered by centrifugation and dried under vacuum: 40.0 mg (27.8  $\mu$ mol, 73%).

$\lambda_{max}$  (nm) ( $\epsilon \times 10^{-4}/L mol^{-1} cm^{-1}$ ) ( $CH_2Cl_2$ ): 277 (9.0) and 352 (2.5).  $\nu_{max}(ATR)/cm^{-1}$  3027, 2963, 1655, 1594, 1544, 1497, 1445, 1393, 1305, 1230, 1193, 1109, 1076, 843, 827, 755, 745, 692, 664 and 612.  $m/z$  (ESI) 1194.28 (M<sup>+</sup>.  $C_{64}H_{44}N_8NdO_8$  requires: 1194.24).

### *Nd(acac)<sub>3</sub>(H<sub>2</sub>O)<sub>2</sub>*:

It is formed by the addition of 3.0 equiv of HAcac to an aqueous solution of  $NdCl_3(H_2O)_6$  with stirring at room temperature. A solution of concentrated (35%)  $NH_3$  is added drop wise until a white precipitate appears. Once no more precipitate is formed, the solid is filtered, washed with water and dried under vacuum to afford the product quantitatively.

### References

- <sup>1</sup> W. H. Meek and C. H. Fuchsmann, *J. Chem. Eng. Data*, 1969, **14**, 388
- <sup>2</sup> J.P Collman, R.R. Gagne, C. Reed, T.R. Halbert, G. Lang and W.T. Robinson, *J. Am. Chem. Soc.*, 1975, **97**, 1427.
- <sup>3</sup> J. Lindsey, *J. Org. Chem.*, 1980, **45**, 5215.
- <sup>4</sup> K.M. Smith, in the "Porphyrins and metalloporphyrins", Ed. Elsevier, 1975.